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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 22 Feb 2010

To cite this article: R. Yamaguchi & S. Sato (2010): Liquid Crystal Material Dependence on Rubbed PVCi Alignment Properties, *Molecular Crystals and Liquid Crystals*, 516:1, 32-37

To link to this article: <http://dx.doi.org/10.1080/15421400903400340>

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Liquid Crystal Material Dependence on Rubbed PVCi Alignment Properties

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We report that the in-plane alignment direction changes by liquid crystal materials on a rubbed polyvinyl-cinnamate (PVCi) film surface. The alignment direction of almost LCs investigated in this study was perpendicular to the rubbing direction. However, a few LCs, for example, MBBA (N-p-methoxybenzylidene p-n-butylaniline) aligned parallel to the rubbing direction. On the other hand, all LCs investigated aligned perpendicular to the polarization direction of the UV light on the photo-alignment PVCi surface. Moreover, the alignment direction of MBBA changed perpendicular to parallel to the rubbing direction with the passage of time after MBBA was put on the irradiated with UV light and subsequently rubbed PVCi surface. These results suggest that the alignment surface is changed by wetting with the LC.

Keywords Alignment direction; nematic liquid crystal; photoalignment; polyvinyl-cinnamate; rubbing

Introduction

Polyvinyl-cinnamate (PVCi) is well known as a photo crosslinkable polymer to align liquid crystal (LC) molecules by a linearly polarized UV (LPUV) light irradiation [1–5]. The LC aligns perpendicular to the polarization direction of LPUV and the alignment mechanism has been discussed. Recently, we have reported that an azimuthal anchoring strength of the rubbed PVCi surface is increased by exposing with an unpolarized UV light over two order magnitude ($10^{-7} \sim 10^{-5}$ N/m) [6]. The multi-domain patterning with different twist angles can be demonstrated by patterning the anchoring strength on the uni-directionally rubbed PVCi surface in the LC cell [7].

Those alignment properties have usually been investigated using 5CB (4-cyano-4'-n-pentylbiphenyl). It has been reported that the 5CB aligns perpendicular to the rubbing direction on the mechanically rubbed PVCi surface, since main-chains are stretched to the rubbing direction and sidechains are oriented perpendicular to the main chains [6,8]. In this study, we used many different types of nematic LC materials and observed those alignment properties on the rubbed

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PVCi surfaces. Then, we found that a few LCs aligned parallel to the rubbing direction. Alignment properties of those LCs were also compared with other LCs on the LPUV surface and the alignment mechanism was discussed.

Experimental

A 4 wt% solution of PVCi was prepared using cyclohexane as a solvent. The solution was spin-coated on an ITO-coated glass or a quartz glass substrate and was baked at 100°C for 10 min. The thickness of the PVCi film was about 100 nm. When the uncrosslinked surface was rubbed, the rubbing strength was reduced to about half comparing to the polyimide film rubbing, since the uncrosslinked surface was soft and the film thickness became less by the usual rubbing strength. We used nematic LC materials more than fifty with different end substances, different cores, as shown in Figure 1. We dissolved a small amount of dichloic dye (G-472 Hayashibara Biochemical Laboratories Inc.) in the LC. The easy axis was checked by observing the absorption anisotropy of the small amount of LC droplet on the PVCi film substrate under the polarized light. The LC at the air interface of the LC droplet aligns perpendicular to the droplet surface [9]. Therefore, the LC droplet becomes the darkest when the substrate surface gives a homogeneous planer alignment and moreover the polarization direction of the incident light coincides with the LC alignment direction. If the LC homeotropically aligns on the substrate surface, the transmission intensity through the LC droplet does not change by rotating the polarizer.

Results and Discussions

All LCs used in this study show the homogeneous planer alignment on the rubbed PVCi surface. Figure 2 shows LC droplet of 5CB, ZLI-4788 (Merck), MBBA (N-p-methoxybenzylidene p-n-butylaniline: Tokyo Kasei Kogyo) and DON-602(DIC). 5CB and ZLI-4788 aligned perpendicular to the rubbing direction, as previously reports. We confirmed that almost other LCs also aligned perpendicular to the rubbing direction. However, only three LCs of MBBA, DON-602 and DON-603 (DIC) were found to align parallel to the rubbing direction.

The homogeneous and homeotropic alignment on a certain polymer surface has been reported using various LC materials [10,11]. When the surface tension of the

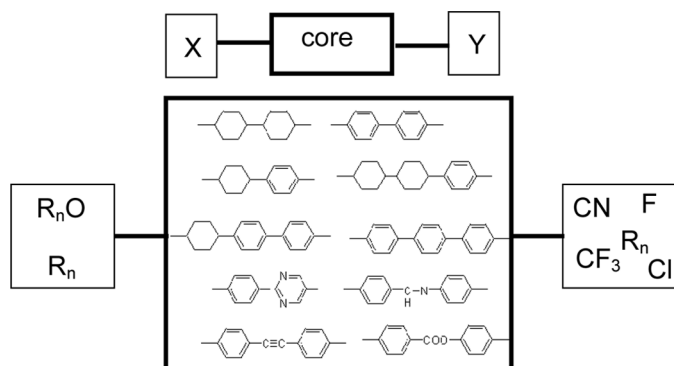


Figure 1. Chemical structures of LCs used in this study.

alignment film is lower (higher) than that of LC, the homeotropic (homogeneous) alignment is observed [10]. To our best knowledge, the change of the in-plane alignment direction in LC materials has not been reported, except the alignment property of a poly-hydroxyethyl methacrylate (pHEMA) surface. Only LCs with bicyclohexane core align perpendicular and other LCs align parallel to the rubbing direction on the rubbed pHEMA surface [10]. Such an alignment property on the rubbed pHEMA is thermally unstable and all LCs align parallel to the rubbing direction when the LC is heat up to the isotropic phase and cool to the nematic phase on the rubbed pHEMA surface. On the other, MBBA, DON-602 and -603 does still align the same direction after the phase transition on the rubbed PVCi surface.

MBBA has a negative dielectric constant and DON-602 and -603 have a neutral dielectric constant. However, ZIL-4788 with a negative dielectric constant aligns perpendicular to the rubbing direction as well as other six LCs with a negative dielectric constant. Therefore, the sign of the dielectric constant dose not contribute to the direction of the alignment direction. MBBA is well known as a single LC of the schiff-base substance. DON-602 and -603, those are the mixture with several kinds of LC substances which does not include schiff-base liquid crystals. Tolane substances must be one of main substances of DON-602 and -603 by supposing the absorption spectrum shown in Figure 3(a). ZIL-4788 also includes the tolane substances and shows the very similar absorption spectrum as shown in Figure 3(b). Therefore, the tolane substance is not dominant factor in the peculiar alignment direction.

Next, we confirmed the alignment direction of MBBA and DON-602 on the LPUV surface. Those LCs aligned perpendicular to the polarization direction of LPUV, as well as 5CB, as shown in Figure 4(a). The mechanism of photoalignment of PVCi has been reported that the LC alignment is mainly induced by the anisotropic orientation of crosslinked sidechains [1,12,13]. This result indicates that the LC alignment function of the crosslinked sidechain is not depend on the LC materials. Moreover, we irradiated the rubbed PVCi surface with unpolarized UV light and observed the LC alignment direction. The alignment direction of this surface is the same as that of only rubbed surface, as shown in Figure 4(b). Uncrosslinked sidechains still orient perpendicular to the rubbing direction by the rubbing treatment and the crosslinked sidechains may also show the anisotropic orientation [2] on the rubbed and subsequently irradiated with the UV light. Therefore, uncrosslinked

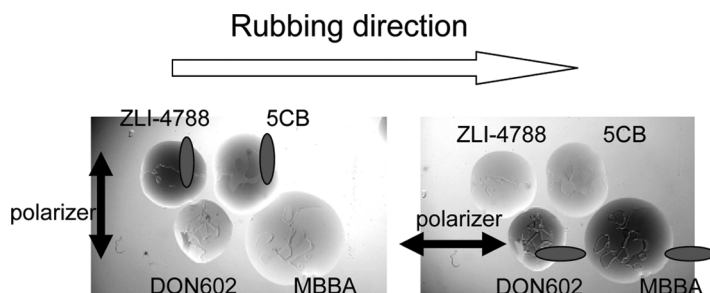


Figure 2. Photographs of LC droplets containing a small amount of dichroic dye on the rubbed PVCi surface.

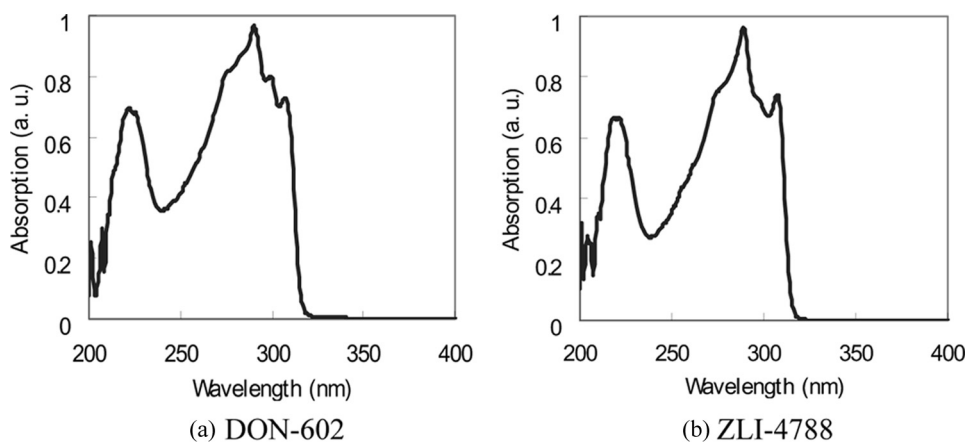


Figure 3. Absorption spectra of (a) DON-602 and (b) ZLI-4788.

sidechain is dominant factor in the LC alignment direction, compared to the crosslinked sidechain on the rubbed surface.

The LC alignment property was still investigated on the PVCi surface which was irradiated with the unpolarized UV light and subsequently rubbed. 5CB aligned perpendicular to the rubbing direction, as well as on the only rubbed surface. MBBA, however, also aligned perpendicular to the rubbing direction just after MBBA was dropped on the surface. Moreover, the alignment direction changed to parallel to the rubbing direction about after 1 minute, as shown in Figure 5. The color of the droplet changed from dark to transparent state with the passage of time and the disclination line simultaneously changed from parallel to perpendicular to the rubbing direction. The descrination line always appears perpendicular to the LC alignment direction through the middle of the droplet, since the tilt direction in the left and

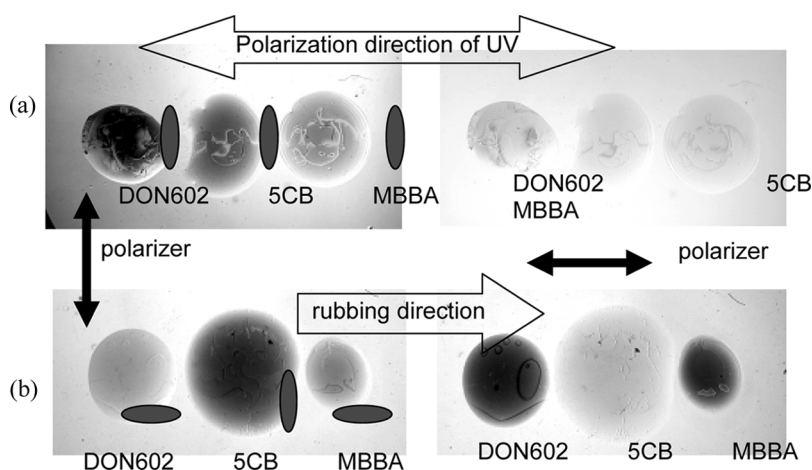


Figure 4. Photographs of LC droplets containing a small amount of dichroic dye on (a) the photoalignment PVCi surface by LPUV irradiation and (b) on the PVCi surface rubbed and subsequently irradiated with the unpolarized UV light.

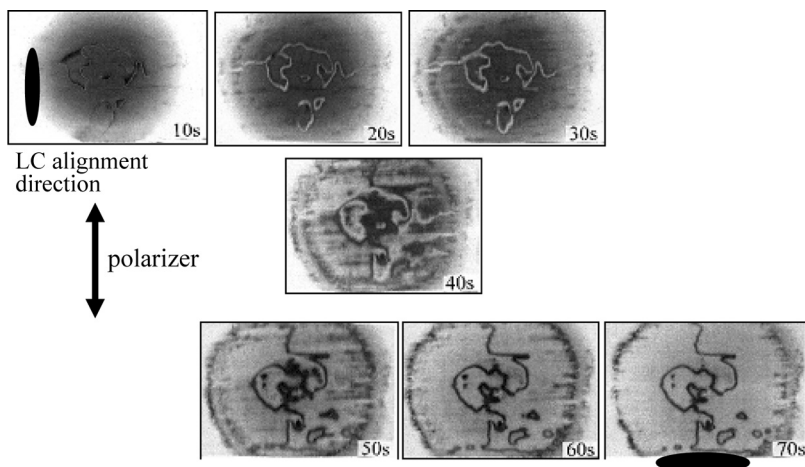


Figure 5. The alignment direction change of MBBA droplets containing a small amount of dichroic dye after MBBA is dropped on the PVCi surface irradiated with the unpolarized UV light and subsequently rubbed.

right half side of the LC droplet is reverse each other on the planer alignment surface [14]. The change was faster under the higher temperature. When MBBA in the isotropic phase was dropped on that PVCi surface and was cooled to the nematic phase, the alignment direction was parallel to the rubbing direction. DON-602 also aligned perpendicular to the rubbing direction and the alignment direction did not change if keeping in the nematic phase. However, it changed to parallel to the rubbing direction when the droplet of DON-602 was heated to the isotropic phase and cooled to the nematic phase.

These results suggest that the LC should change the orientation of PVCi molecules. For the rubbing-induced orientation of the PVCi sidechains, it has been reported that sidechains are out of the surface and the plane of those phenyl rings appear normal to the rubbing direction. Therefore, the oriented phenyl rings align

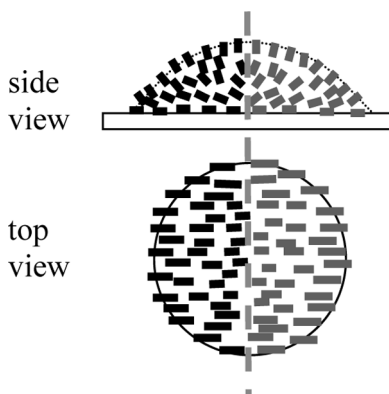


Figure 6. The schematic model of the LC alignment in the LC droplet on the planer alignment surface. The broken line shows a reverse tilt disclination line (wall).

the LC perpendicular to the rubbing direction through the π - π interaction with the rings of the LC molecules [15]. If the phenyl plane of PVCi sidechains would change to parallel to the rubbing direction or the connecting angle of the sidechain along mainchains would change by wetting with MBBA and DON-602, those LCs align parallel to the rubbing direction. The molecular orientation of PVCi sidechains should be studied under the wetting state with the LC, not at an air interface.

Summary

Many kinds of LCs investigated in this study aligned entirely perpendicular to the polarization direction of LPUV photoalignment PVCi surface. However, on the rubbed PVCi surface, MBBA and DON-602 and -603 were found to align parallel to the rubbing direction, even if almost LCs more than fifty aligned perpendicular to the rubbing direction. In addition, the alignment direction of MBBA changed perpendicular to parallel to the rubbing direction with the passage of time on the irradiated with UV light and subsequently rubbed PVCi surface. The change was faster under the higher temperature. These results suggest that the molecular orientation of PVCi sidechains is changed by wetting with the LC.

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