Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Hong, Sung-Kyu , Kikuchi, Hirotsugu and Kajiyama, Tisato(2000) 'Preliminary communication:Novel method for uniform orientation of liquid crystal molecules by a polyimide surface exposed to a water flow', Liquid Crystals, 27: 4, 547 — 550

To link to this Article: DOI: 10.1080/026782900202732
URL: http://dx.doi.org/10.1080/026782900202732

LIQUID CRYSTALS, 2000, VOL. 27, NO. 4, 547–550

Preliminary communication

Novel method for uniform orientation of liquid crystal molecules by a polyimide surface exposed to a water flow

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(*Received 18 June 1999; in final form 23 September 1999; accepted 12 October 1999*)

A novel technique for surface-induced orientation of liquid crystal (LC) molecules is proposed, using a polyimide surface exposed to a unidirectional water flow. The LC molecules director was unidirectionally oriented along the water flow direction on the polyimide surface. The orientational state of the LC director was strongly dependent upon whether the water flow exposure was carried out before or after thermal curing for imidization, and also upon the temperature of water flow.

A polymer surface rubbing treatment is generally carried out to obtain a uni-axially oriented mono-domain state of the LC molecule director in the fabrication of liquid crystal display (LCD) panels. The director is uni-axially oriented parallel to the rubbing direction of the polymer surface by contact with the rubbed polymer surface. Berremann proposed, on the basis of LC elastic theory, that the LC director is oriented along the surface grooves created in the rubbing process [1]. Recently, it has been reported that the director orientation may be induced by the orientation of chemical groups on the rubbed polymer surface, even though the orientation mechanism of LC molecules is not yet well understood [2–4].

Several non-contacting fabrication processes have been proposed for orientation of the polymer surface, since there are several serious disadvantages in the rubbing process, such as a static charge formation or dust generated by contact between the polymer surface and the rayon velvet of the rubbing roller. A number of non-rubbing processes have therefore been proposed; for example, polymer surface irradiation by linearly polarized light [5–10], the Langmuir-Blodgett method [11] or a microwave groove method [12]. However these methods have not been applied as commercial fabrication techniques to LCD production, due to reduced reproducibility or high production costs. The optical alignment method is one promising method for control of the molecular alignment of liquid crystals; however, there has been much delay in putting this method into practice, because of low manufacturing efficiency.

It is reported that a slight orientation imposed in a poly(amic acid) film (as a precursor of polyimide) is significantly amplified by thermal imidization [13]. Thus, even if the orientational order induced by a surface treatment of the poly(amic acid) was quite small, a highly ordered polyimide orientation was obtained by a strong amplification effect during the curing process.

In this study the dependence of the LC director orientation on curing treatment and water temperature is discussed, using a polyimide surface which has been exposed in a unidirectional water flow at varying temperature. Figure 1 shows the chemical structures of poly(amic acid) and polyimide [poly(3,3′,4,4′-biphenyltetracarboxylic dianhydride-*p*-phenylenediamine), BPDA-PDA, Unitica Co. Ltd.]. BPDA-PDA was prepared by thermal curing of BPDA-PDA acid. Figure 1 also shows the chemical structure of the nematic LC 4-cyano-4′-*n*-pentylbiphenyl (5CB, Merck Ltd.).

The scheme shows the fabrication process of a sandwich-type LC cell composed of two substrates coated with BPDA-PDA. The BPDA-PDA acid film was prepared by spin-coating (4000 rpm) a *N*-methylpyrrolidone (NMP) solution onto glass substrates at 288 K; the NMP was then evaporated from the poly(amic acid) film in a vacuum oven at 313 K for 1 h. In the case of polyimide sandwich LC cell (A), each substrate inner surface was covered with BPDA-PDA acid film without

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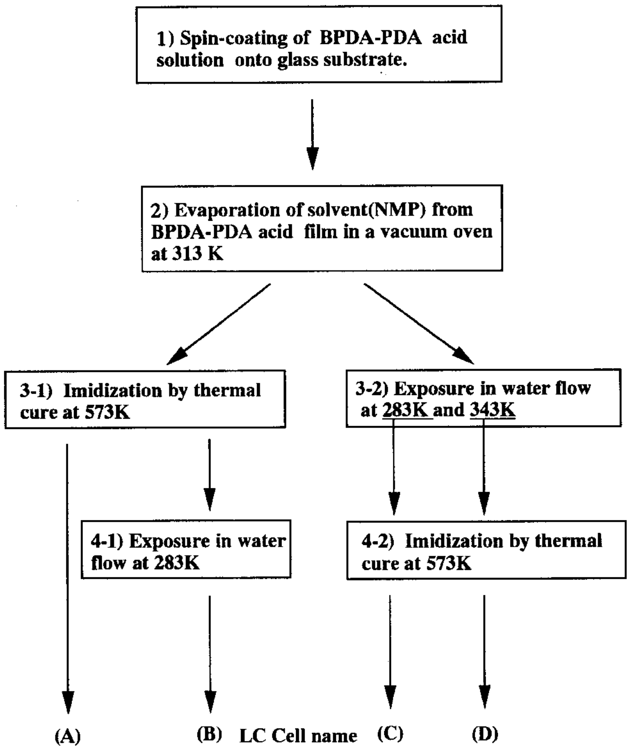
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals/tf/02678292.html



Scheme. Fabrication method for the sandwich LC cell composed of two substrates coated with BPDA-PDA.

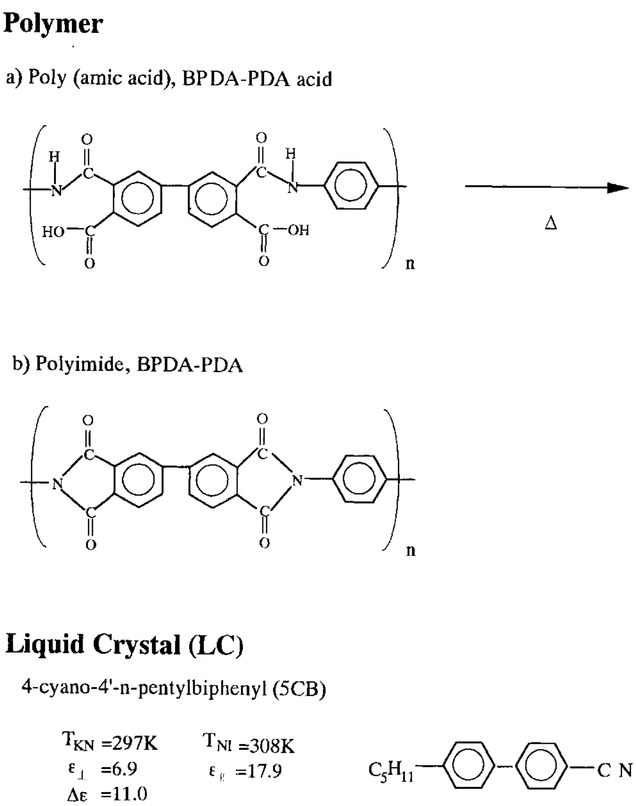


Figure 1. Chemical structures and physical properties of the polymer and LC used in this study.

any water flow treatment, and then the BPDA-PDA acid film was converted into the BPDA-PDA film by thermal curing in a vacuum at 573 K for 2 h. To obtain the LC cell (B), the BPDA-PDA film surface was also exposed to a unidirectional water flow. On the other hand, in the cases of LC cells (C) and (D), BPDA-PDA acid film surfaces were exposed in a unidirectional water flow at 283 K and 343 K for 10 s, respectively; the BPDA-PDA acid films were then converted into BPDA-PDA films by thermal curing under the same conditions as LC cells (A) and (B), respectively. The cells (B), (C) and (D) were assembled so that the directions of water flow on the two substrates were parallel, to investigate the effect of (a) processing order of imidization and (b) water flow treatment, on the surface orientation. Finally, each cell was filled with 5CB in an isotropic phase. The LC thickness was set at 14 μm by use of a PET film spacer. The water flow rate was 0.4 m s^{-1}. The resulting LC molecule orientational state and the light transmittance intensity (I) dependence on sample rotation angle (ϕ), for each LC cell, were evaluated at 300 K with a polarized optical microscope (POM) under crossed Nicols. The rotation axis of the same was normal to the substrate surface of the cell. $\phi = 0$ corresponds to the flow direction of the water. The $I(\phi)$ was normalized against I at $\phi = \pi/4$, $I(\pi/4)$.

Figures 2 and 3 show POM photographs and normalized light transmittance, $I(\phi)/I(\pi/4)$ respectively, for 4 kinds of LC cell at 300 K. Figure 2 (*a*) shows the orientational state of LC cell (A) whose surface was not treated by any water flow. Although the bright field of the nematic texture was observed, as shown in figure 3 (*a*), the magnitude of $I(\phi)/I(\pi/4)$ was almost constant for the rotation of the LC cell (A) about the substrate surface normal. This apparently indicates that the orientation of the LC director in the cell (A) was random in plane. Figure 2 (*b*) shows the POM photograph for the LC cell (B) whose BPDA-PDA film surface was exposed to water flow after imidization by thermal curing at 573 K. A partial uniform bright field of the nematic texture was observed, as shown in figure 2 (*b*), and the magnitude of $I(\phi)/I(\pi/4)$ changed periodically with every $\pi/2$ of ϕ as shown in figure 3 (*b*). However, the transmittance was not zero at 0, $\pi/2$ and π. This indicates that the LC director oriented partially along the direction of water flow but, the orientation of LC molecules was not complete. Figures 2 (*c*) and 2 (*d*) show POM photographs for the LC cells (C) and (D), respectively, whose BPDA-PDA acid film surfaces were exposed to water flow at 283 K and 343 K respectively, before imidization by thermal curing at 573 K. Although a number of elongated defects was observed in the case cell (C), the LC molecule director was partially oriented along the direction of water flow, as shown in figures 2 (*c*) and 3 (*c*). On the other hand,

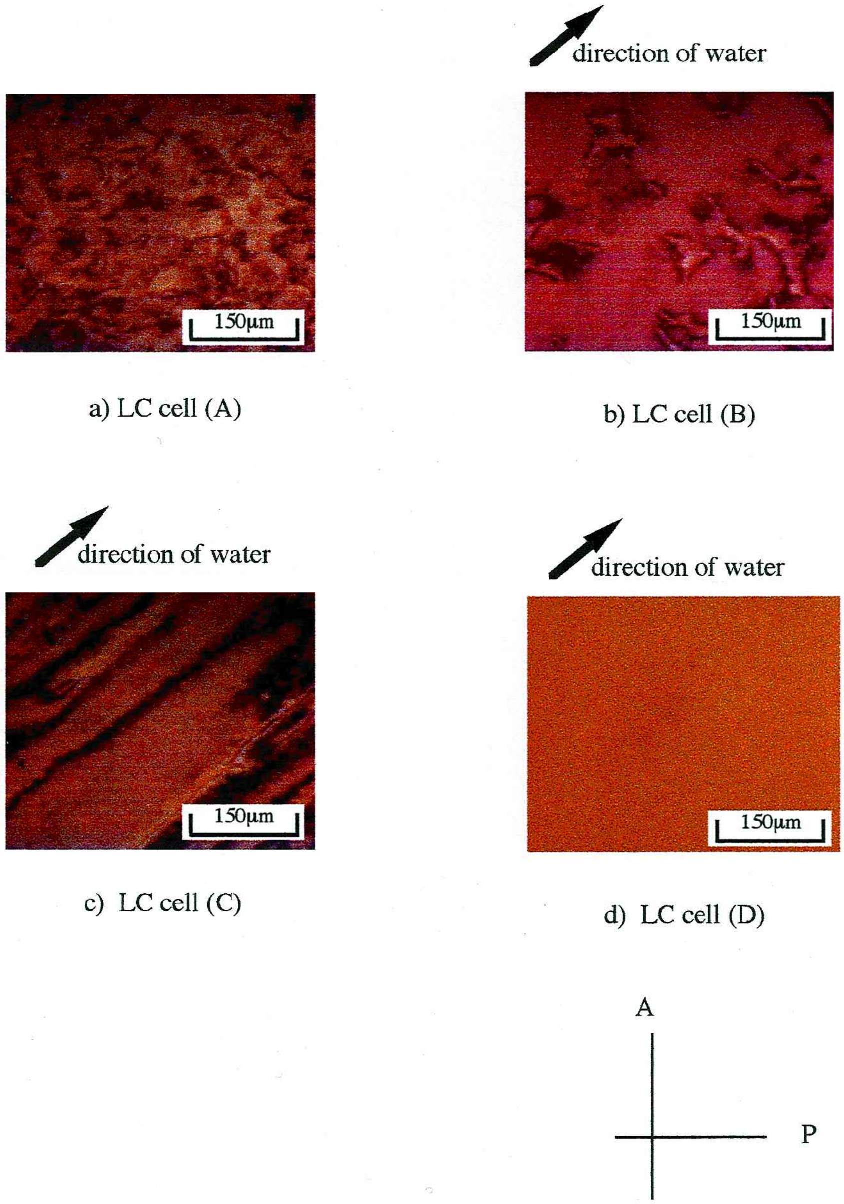


Figure 2. POM-observation photographs for the four types of LC cell at 300 K under crossed Nicols.

in the case of cell (D), a perfect mono-domain of the nematic phase was observed, as shown in figure 2 (*d*). Also, the magnitude of $I(\phi)/I(\pi/4)$ changed periodically with every $\pi/2$ of ϕ and was nearly zero at 0, $\pi/2$ and π, as shown in figure 3 (*d*). The variation of light transmittance in figure 3 (*d*) follows equation (1):

$$\frac{I(\phi)}{I(\pi/4)} = \sin^2 \phi. \qquad (1)$$

These results indicate that the LC director is uniformly oriented along the direction of water flow in the case of the LC cell (D). It was expected from figures 2 and 3 that the water flow induced a light orientation of chemical groups along the flow direction, due to a laminar flow of water on the surface of BPDA-PDA acid and BPDA-PDA. It has been reported that as-cast BPDA-PDA acid, and BPDA-PDA after thermal imidization, are amorphous and semicrystalline, respectively [13, 14]; also, that the well-oriented crystalline structure of BPDA-PDA is induced by thermal imidization of BPDA-PDA acid film which is slightly stretched. Thus it seems reasonable to consider that the orientational order of BPDA-PDA acid might be remarkably amplified during the thermal curing process from poly(amic acid) to polyimide, as shown in the cases of cells (C) and (D).

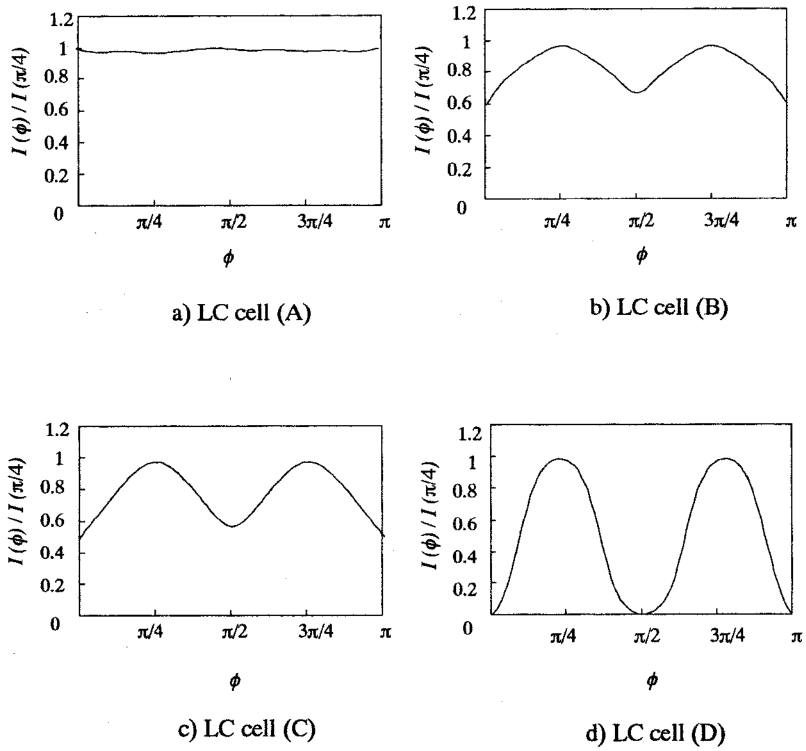


Figure 3. $I(\phi)/I(\pi/4)$ against ϕ for the four types of LC cell at 300 K under crossed Nicols.

Furthermore, the results for cells (C) and (D) indicate that a molecular rearrangement or an orientation of the BPDA-PDA acid chains was easier at the higher water flow temperature. That is, the LC molecule director was more uniformly oriented along the direction of water flow because a more highly oriented polymer chain was obtained with increase of water temperature. Therefore, it may be possible to control the nematic LC director by the polyimide surface exposed to water flow at an appropriate temperature.

In the case that the poly(amic acid) was exposed to the water flow and was then thermally cured at 573 K to obtain the polyimide film, the LC molecule director became unidirectionally oriented along the direction of water flow on the polyimide surface. The orientational state of the LC director was strongly dependent upon whether the water flow treatment on the polymer surface was carried out before or after thermal imidization of the poly(amic acid), and also upon the temperature of water flow. It can be concluded that water flow treatment of the polymer surface is applicable as a novel technique to obtain a surface-induced orientation of LC molecules as an alternative to a conventional rubbing treatment.

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