

Photo-driven liquid crystal cell with high sensitivity

LI CUI, PING XIE*†, RONGBEN ZHANG*†

Polymer Chemistry Laboratory,
 Chinese Academy of Sciences and China Petro-chemical Corporation,
 Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080,
 PR China

and TONGHUA YANG*

Chinese Institute of Atomic Energy, Beijing 102413, PR China

(Received 24 March 1999; accepted 19 April 1999)

The photo-driven LC cell was assembled by sandwiching the liquid crystal material between two quartz or ITO plates covered with a 'command layer', which was fabricated from azobenzene-grafted ladder-like polysilsesquioxanes. The improved response sensitivity of the photo-driven cell, which means a lower threshold driving UV light intensity and a faster rise-time, was achieved in two ways: pre-rubbing of the command surface and application of an assisting critical in-plane mode electric field. The response behaviour of the photo-driven cell was measured *in situ* and data were collected by computer. The results show that the rise-time (4 s) under a weak UV intensity of 0.5 mWcm^{-2} is shorter than previously reported (several tens of seconds) under a greater UV intensity of $3\text{--}5 \text{ mWcm}^{-2}$. The improved photo-driven LC cell holds out promise of potential applications in photo-addressing and photo-recording.

1. Introduction

Compared with the conventional liquid crystal display (LCD) driven by an electric field, the novel LCD mode driven by long wave length UV light is based on the fact that azobenzene (Az) derivatives can undergo optically induced *trans/cis*-isomerization [1–3] that makes them applicable for controlling the alignment of surrounding liquid crystal (LC) molecules. Photoisomerization of photochromic molecules is a fast process: transient absorption spectroscopy shows that the *trans/cis*-photoisomerization of Az derivatives can be complete within 10 ns [4]. From this point of view, the LC cell driven by Az units on a command surface offers a new way to construct LC display devices. Eich and Wendorff, and Ichimura *et al.* [2, 5] first investigated the reversible changes of homeotropic and parallel alignment of LCs induced by the isomerization of Az units on a so-called 'command surface'. In-plane homogeneous alignments and azimuthal alterations of LCs triggered by the action of linearly polarized light (LPL) in azobenzene [6–8] and spiro-pyran [9] monolayer-controlled systems were also reported and could be used for photo-image recording. In previous reports, we have investigated

photo-driven LC cells based on the Az units grafted onto ladder-like polysilsesquioxanes as the command layer and the response behaviour [10, 11]. The experimental results showed that the photo-driving behaviour is strongly dependent on the nature of the LCs, as well as on the structure of the Az side groups.

On the other hand, the pre-orientation status of liquid crystals plays a particularly important role in the performance of LCDs and this status is strongly dependent on the nature of the substrate surface [12–14]. Practically, unidirectional rubbing of polymer films on substrates is commonly used to control the director of the LC and a pre-tilt angle between the LC director and the substrate plane, generally of $1^\circ\text{--}4^\circ$ is required to overcome reverse tilt which obviously deteriorates the displayed images. In the case of the supertwisted nematic (STN) mode display, a higher pre-tilt of about $5^\circ\text{--}8^\circ$ is preferable for the avoidance of two dimensional stripe instabilities [15] and is essential for the realization of stable highly twisted configurations exhibiting very steep transmission-voltage characteristics [16]. For the photo-driven LC cell in which the LC alignment turns from homeotropic to planar triggered by radiation of long wave-length UV light, a suitable tilt from the vertical direction may be helpful in eliminating disturbance between adjacent LC molecules.

* Author for correspondence.

† e-mail: caoming@public.east.cn.net

In the commercial twisted nematic (TN) and super-twisted nematic (STN) mode LCDs, the display is achieved by the response of the LC to an electric field applied perpendicular to the substrates. Recently, the in-plane switching (IPS) mode LCD has been reported as a promising approach to improving the viewing angle characteristics [17–19]. In this case, the electric field is provided along a direction parallel instead of perpendicular to the plane of the substrates by using interdigital electrodes.

This report aims to improve the response sensitivity of the photo-driven cell by pre-rubbing of the command surface and applying an assisting critical electric field; this has resulted in a lower threshold UV light intensity for driving the cell and a shorter rise time.

2. Experimental

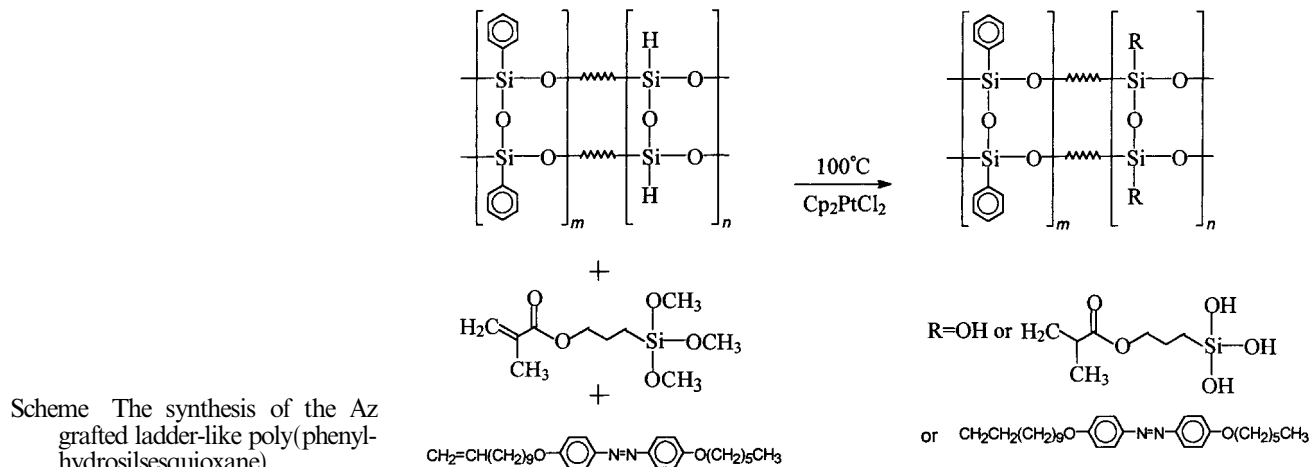
2.1. Materials

The nematic liquid crystals, 4-pentyl-4'-cyanobiphenyl (5CB) (transition temperature: nematic–isotropic $T_{NI} = 35^\circ\text{C}$) and TEB-30 ($T_{NI} = 65^\circ\text{C}$), were purchased from the Liquid Crystal Materials Company of Tsinghua University (Beijing, China); their structures are given in ref. [11]. 3-Trimethoxysilyl-propyl methacrylate (KH-570) is a commercially available coupling agent. 4-Hexyloxy-4'-undecenyloxyazobenzene (6Az11) was prepared according to our previous reports [20, 21].

2.2. Synthesis

The skeleton material, a ladder-like copoly(phenyl-hydrosilsesquioxane) (PPHSQ) with a phenyl/H mol ratio of 70:30, was synthesized as before [20].

The film-forming material, P-6Az11-KH570 (PPHSQ grafted with 6Az11 and KH-570) was synthesized by hydrosilylation reaction, as shown in the scheme.



Scheme The synthesis of the Az grafted ladder-like poly(phenyl-hydrosilsesquioxane).

A Schlenk flask was degassed three times with dry argon. Then, 2 ml of a toluene solution (concentration 45 mg ml^{-1} ; Si-H: $0.135 \text{ mmol ml}^{-1}$) of PPHSQ, 9 ml of anhydrous toluene, 20 mg of 6Az11, 10 mg of KH-570, and 0.2 ml of a dichloromethane solution (concentration: 1 mg ml^{-1}) of dicyclopentadienylplatinum dichloride (Cp_2PtCl_2) as catalyst were injected. The system was stirred at 100°C for 48 h under the protection of dry argon. In this way, PPHSQ grafted with 6Az11 and KH-570 (P-6Az11-KH570), was prepared.

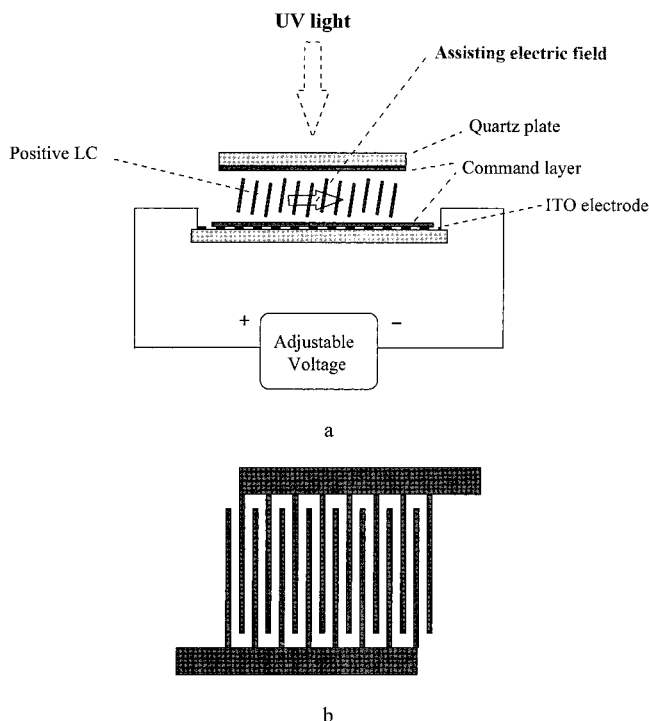


Figure 1. A schematic representation of the cell assembly with a critical assisting electric field in IPS mode: (a) cell assembly; (b) the pattern of interdigital ITO electrodes.

2.3. Film preparation, rubbing and cell assembly

A 0.8% toluene solution of P-6Az11-KH570 was spin coated on cleaned glass plates at 1500 rpm to form a thin polymer film, which was then annealed at 180°C for 4 h. The rubbing treatment was carried out by pressing the polymer-coated plate down onto a moving velvet cloth as described in ref. [22]. The loading pressure was 2.5 g cm^{-2} , and the velvet cloth was moved unidirectionally at a velocity of 2 mm s^{-1} over a distance of 1.5–3 m.

A cell was assembled using an 8 μm -thick polyethylene film as spacer between two quartz plates whose rubbing directions were anti-parallel. The liquid crystal TEB-30 was filled in by capillary action at 70–80°C. The cell, to which an assisting critical electric field can be applied, was assembled with one quartz plate as the upper plate and one ITO glass plate etched as an interdigital

electrode as the lower plate, as shown in figure 1. The electric field was controlled at a 'critical' value which cannot drive the LC molecules to realign. The photo-optical response of the cell was measured *in situ* by the system shown in figure 2.

2.4. Measurements

The cell was observed by a Xintian XP1A (China) polarizing optical microscope. The conoscopic picture was obtained using crossed polarizers with a condensing lens and an inserted Bertrand lens, a sodium lamp acting as the monochromatic light source.

The response behaviour of the photo-driven cell was measured using a 375 W mercury UV lamp as the driving light source, a laser diode providing a light source for the detecting system. The transmitted light was detected by a photo-diode and the data were collected by computer.

3. Results and discussion

3.1. Pre-tilt of the liquid crystals

In previous research on photo-driven LC cells, the initial alignment of the LC is purely homeotropic; in other words, the long axes of the LC molecules are vertical to the plane of the plate. Under the triggering effect of the UV light, such a homeotropic state turns to a disordered planar alignment with many defects due to reversed tilt, as shown in figure 4(a).

In this study, the P-6Az11-KH570 polymer film was slightly rubbed over a distance of 1.5–3 m under a loading pressure of 2.5 g cm^{-2} . The LC molecules in the cell are pre-aligned with some tilt from the vertical direction. Such alignment is confirmed by the conoscopic images shown in figure 3. Under conoscopic conditions, dark Maltese crosses with different eccentricities were observed for different rubbing strengths. A tilted homeotropic alignment of the LCs was therefore induced by the

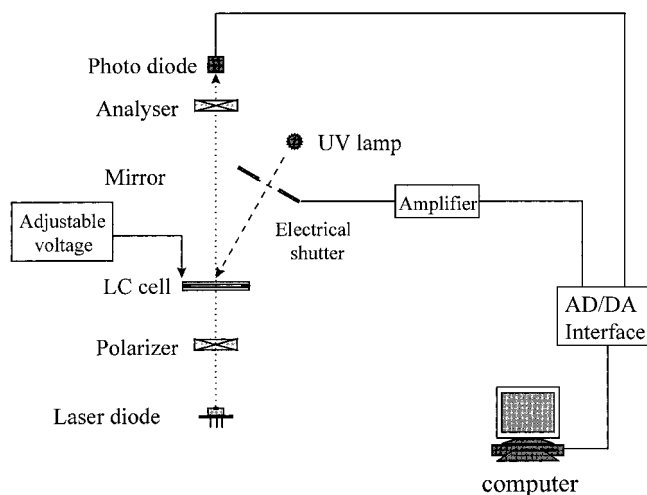


Figure 2. The system used to determine the photo-optical response.

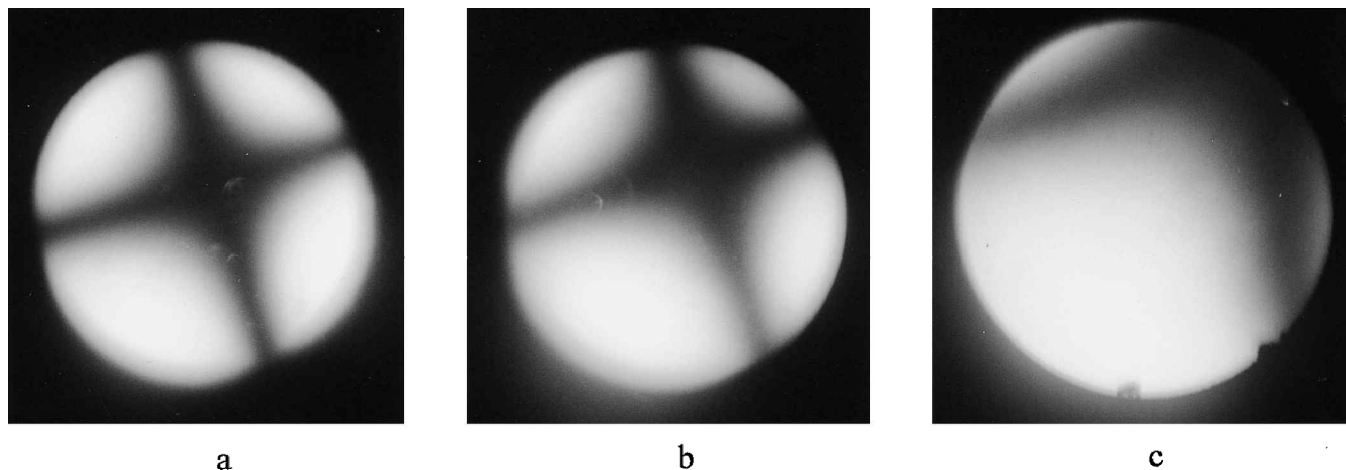


Figure 3. Conoscopic pictures of the cell assembled with the P-6Az11-KH570 modified plates rubbed under pressure $3 \sim 5 \text{ g cm}^{-2}$ over different rubbing distances: (a) 1.5 m; (b) 2.1 m; (c) 3 m.

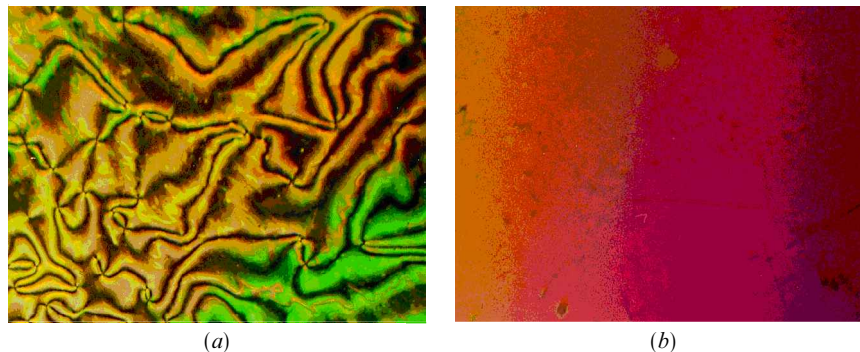


Figure 4. The polarized light photo-micrographs of the cells assembled with slightly rubbed and non-rubbed plates under UV drive in the homogeneous state: (a) non-rubbed; (b) rubbed over 3 m under a pressure of 2.5 g cm^{-2} .

'pre-rubbing' process. When the tilted homeotropic state was triggered by UV light, the LC molecules turned parallel to the rubbing direction. Therefore a uniform homogeneous alignment can be obtained as shown in figure 4(b).

3.2. Photo-optical response of the cells by the 'pre-tilt' process

The photo-optical responses of the cells assembled with slightly rubbed plates under different UV intensities are shown in figure 5; the transmittance of the cell between crossed polarizers was recorded *in situ* when the cell was exposed to UV light. The rise-time is about 12 s when the cell is exposed to a UV intensity of 1 mW cm^{-2} , and the off-time is about 40 s.

The pre-tilt process can improve the sensitivity of the photo-driven LC cell. In our previous reports [10, 11], the intensity of the UV light was about $3\text{--}5 \text{ mW cm}^{-2}$ and the response time was several tens of seconds. Compared with this work, the response of the cell assembled with non-rubbed plates under a UV light intensity of 1 mW cm^{-2} was recorded as shown in figure 6. The rise-time was about 44 s and the off-time about 60 s. It is obvious that the response of the cell assembled with the pre-rubbed plates is faster than that of the cell assembled with non rubbed plates.

3.3. Photo-optical response of photo-driven cell with critical electric field

The photo-driven LC cell with a critical electric field was assembled using two polymer-modified and pre-rubbed plates, but the lower plate is ITO glass etched as an interdigital electrode instead of a quartz plate shown as in figure 1. When a d.c. potential of 5.3 V was applied to the cell, the LC molecules began to change alignment at the boundary of the electrode. Therefore, a d.c. potential of 5 V was adopted for the critical potential. Figure 7 shows the response of the cell with an assisting critical potential of 5 V and exposed to UV of 0.5 mW cm^{-2} .

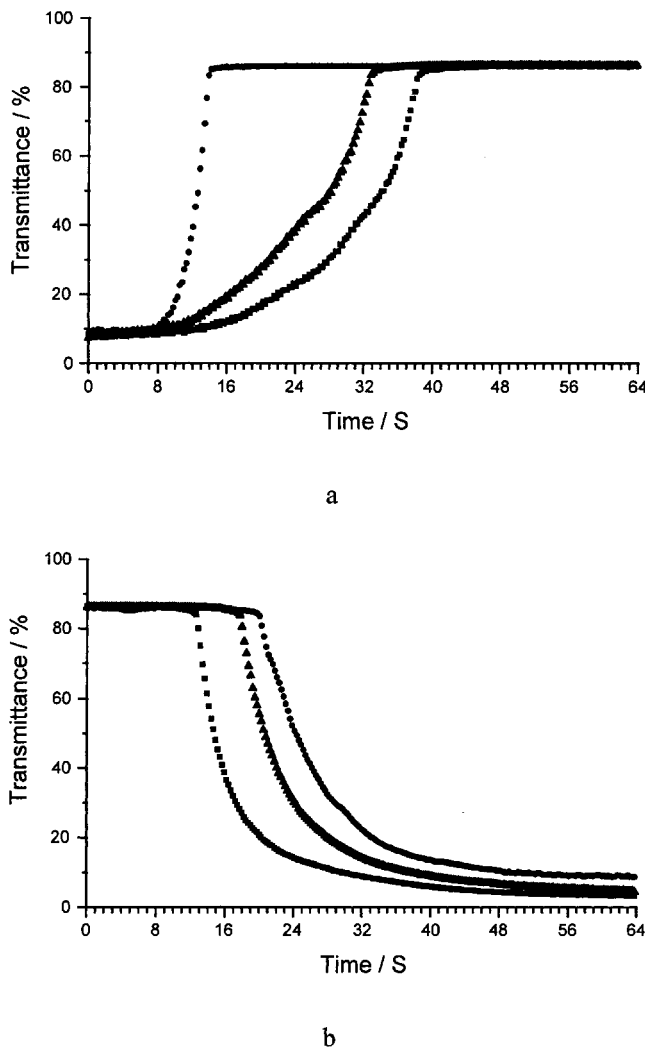
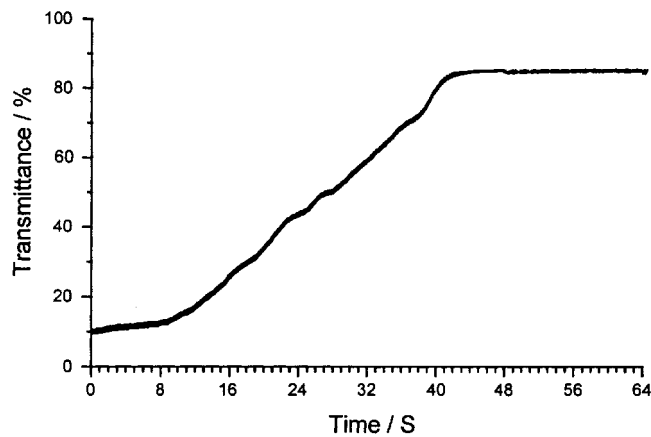
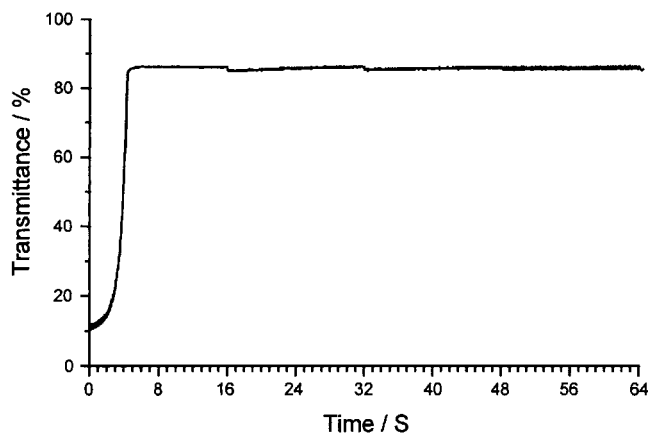


Figure 5. The photo-optical response of the cell assembled with slightly rubbed plates under different UV intensities (\bullet 1 mW cm^{-2} , \blacktriangle 0.7 mW cm^{-2} , \blacksquare 0.5 mW cm^{-2}) at 25°C : (a) driving 'on' process; (b) 'off' process.

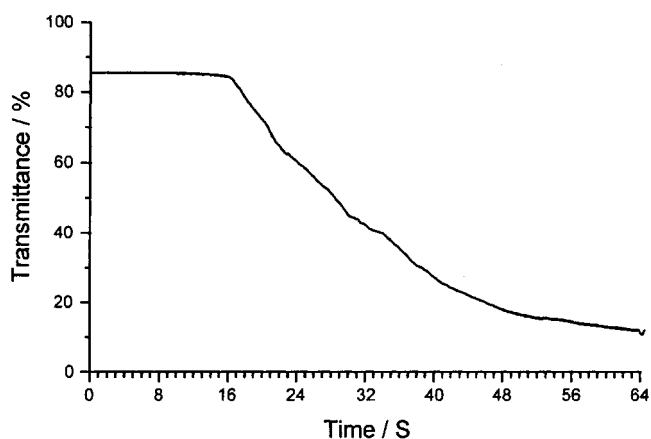
As shown in figure 7(a), the driving 'on' process is fast and the rise-time is about 4 s; the off-time is about 60 s. This indicates that the critical potential applied to



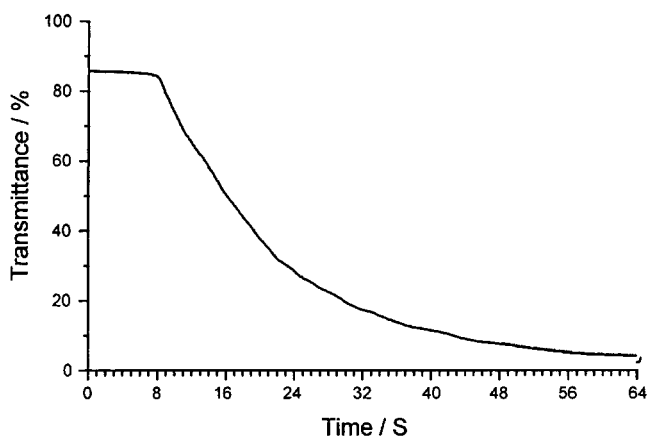
a



a



b



b

Figure 6. The photo-optical response of the cell assembled with non-rubbed plates under UV light intensity of 1 mW cm^{-2} : (a) driving 'on' process; (b) 'off' process.

Figure 7. The photo-optical response of the cell assembled with slightly rubbed plates (loading pressure 2.5 g cm^{-2} over a distance of 3 m) and a 5 V assisting critical potential applied to the LC cell; the intensity of the UV light is 0.5 mW cm^{-2} : (a) driving 'on' process; (b) 'off' process.

the cell can accelerate the process that changes the LC alignment from a homeotropic state to a planar alignment state triggered by UV light, but it hinders the LC molecules from recovering to the homeotropic alignment when UV light exposure is stopped.

4. Conclusion

The sensitivity of the photo-driven LC cell was improved in two ways: a pre-rubbing treatment and by applying an assisting critical electric field. The pre-rubbing treatment can not only lower the driving UV intensity and quicken the response time, but also can induce a uniform homogeneous alignment when triggered by UV light. Hopefully, the results hold out promise of potential applications of photo-driven LC cells in areas such as photo-addressing and photo-recording.

This work was supported by the National Natural Science Foundation of China (grant No. 29574187 & 2967400) and PCLCC (Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petrochemical Corporation).

References

- [1] ANDERLE, K., BIRENHEIDE, R., EICH, M., and WENDORFF, J. H., 1989, *Makromol. Chem., rapid Commun.*, **10**, 477.
- [2] EICH, M., and WENDORFF, J. H., 1987, *Makromol. Chem., rapid Commun.*, **8**, 467.
- [3] ICHIMURA, K., SUZUKI, Y., and SEKI, T., 1988, *Langmuir*, **4**, 1214.
- [4] KURIHARA, S., IKEDA, T., SASAKI, T., KIM, H. B., and TASUKE, S., 1990, *J. chem. Soc., chem. Commun.*, 1751.

- [5] AOKI, K., SEKI, T., SUZUKI, Y., TAMAKI, T., HOSOKI, A., and ICHIMURA, K., 1992, *Langmuir*, **8**, 1007.
- [6] ICHIMURA, K., HAYASHI, Y., and AKIYAMA, H., 1993, *Langmuir*, **9**, 3298.
- [7] STUMPE, J., MULLER, L., KREYSIG, D., HAUCK, G., KOSWIG, H. D., RUHMANN, R., and RUBNER, J., 1991, *Makromol. Chem., rapid Commun.*, **12**, 81.
- [8] ICHIMURA, K., 1994, *Mol. Cryst. liq. Cryst.*, **246**, 331.
- [9] ICHIMURA, K., HAYASHI, Y., and ISHIZUKI, N., 1992, *Chem. Lett.*, 1063.
- [10] TANG, YX., LIU, DS., XIE, P., and ZHANG, RB., 1996, *Makromol. Chem., rapid Commun.*, **17**, 759.
- [11] TANG, YX., XIE, P., LIU, DS., ZHANG, RB., ZHANG, ZY., and YAO, NY., 1997, *Macromol. chem. Phys.*, **198**, 1855.
- [12] COGNARD, J., 1982, *Mol. Cryst. liq. Cryst., Suppl. Ser.*, **1**, 1.
- [13] CUI, L., JIN, W., LIU, JN., TANG, YX., XIE, P., and ZHANG, RB., 1998, *Liq. Cryst.*, **25**, 757.
- [14] CUI, L., JIN, W., LIU, YB., XIE, P., and ZHANG, RB., 1999, *Mol. Cryst. liq. Cryst.* (in the press).
- [15] RAJA, V., SHANKAR RAO, D., KANG, S., LEE, J., LEE, S., and JIN, S., 1996, *Liq. Cryst.*, **20**, 41.
- [16] SCHADT, M., SEIBERLE, H., and SCHUSTER, A., 1996, *Nature*, **381**, 212.
- [17] BAUR, G., KAMM, M., KLAUSMANN, H., WEBER, B., and WINDSCHEID, F., 1994, in Abstracts of the 15th International Liquid Crystal Conference, Abstr. K-P15.
- [18] BAUR, G., 1993, *Freiburger Arbeitstagung Flussigkristalle*, Abstr. 22.
- [19] OH-E, M., and KONDO, K., 1997, *Liq. Cryst.*, **22**, 379.
- [20] XIE, ZS., JIN, SZ., WAN, YZ., and ZHANG, RB., 1992, *Chin. J. polym. Sci.*, **10**, 361.
- [21] ZHANG, SY., BI, SW., XIE, P., and ZHANG, RB., 1991, *Chin. J. polym. Sci.*, **9**, 195.
- [22] KIKUCHI, H., LOGAN, J. A., and YOON, D. Y., 1996, *J. appl. Phys.*, **79**, 6811.