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

A novel vertical alignment technology for nematic liquid crystals based on electrostatic self-assembled method

Lishuang Yao[ab]; Limei Shao[c]; Zenghui Peng[a]; Lingli Zhang[ab]; Chunhong Fei[ab]; Fengzhen Lv[ab]; Li Xuan[a]
[a] State Key Laboratory of Applied Optics, Changchun Insititute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, P. R. China [b] Graduate School of Chinese Academy of Sciences, Beijing, P. R. China [c] Public Education and Research Center of Physics, Jilin University, Changchun, P. R. China

To cite this Article Yao, Lishuang , Shao, Limei , Peng, Zenghui , Zhang, Lingli , Fei, Chunhong , Lv, Fengzhen and Xuan, Li(2007) 'A novel vertical alignment technology for nematic liquid crystals based on electrostatic self-assembled method', Liquid Crystals, 34: 6, 761 — 765

To link to this Article: DOI: 10.1080/02678290701342945

URL: http://dx.doi.org/10.1080/02678290701342945

Liquid Crystals, Vol. 34, No. 6, June 2007, 761–765

A novel vertical alignment technology for nematic liquid crystals based on electrostatic self-assembled method

LISHUANG YAO*†‡, LIMEI SHAO§, ZENGHUI PENG†, LINGLI ZHANG†‡, CHUNHONG FEI†‡, FENGZHEN LV†‡ and LI XUAN†

†State Key Laboratory of Applied Optics, Changchun Insititute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dongnanhu Road, Changchun, 130033, P. R. China
‡Graduate School of Chinese Academy of Sciences, Beijing, 100049, P. R. China
§Public Education and Research Center of Physics, Jilin University, Changchun, 130021, P. R. China

(*Received 8 January 2007; accepted 27 February 2007*)

A novel vertical alignment film for nematic liquid crystals is reported based on electrostatic self-assembly of alkyl sulfonic salts in aqueous solution. A series of self-assembled films with different alkyl chain lengths were prepared and used as alignment films. It was revealed that only when the number of carbon atoms in the alkyl chain approaches 11 or larger, could the self-assembled film induce vertical alignment of liquid crystals. We also found that the homeotropic alignment of liquid crystals was related to the surface roughness of self-assembled films. In addition, this vertical alignment film showed good electro-optical characteristics and excellent thermal stability.

1. Introduction

Liquid crystal displays (LCDs) have been extensively employed because of their distinct advantages, e.g. good display quality, facile fabrication, flicker-free operation and low power consumption [1]. Hence, work on LCDs has attracted much attention as a field of research. Accordingly, various types of LCDs have been presented, such as twisted nematic (TN), in-plane switching (IPS), and vertical aligned (VA) mode, and so on [2–4].

The VA mode LCD exhibits an excellent contrast ratio, fast response time and weak colour dispersion. Hence, this type of LCD is widely used for direct-view and projection displays, and has attracted much research attention [5].

Of course, most LCDs require alignment layers to achieve a preferential orientation direction of the liquid crystals. The alignment film for conventional VA-LCDs mostly focuses on rubbed polyimide (PI) film with long alkyl chains. However, the PI alignment film needs complex operation of thermal imide reaction at rather high temperature, which may be harmful for the integrated circuit. Also, the rubbing process of PI alignment film induces some drawbacks for liquid crystals devices, such as dirt contamination, static charge generation and scratching [6]. Furthermore, many researchers have adopted the photo-alignment technique to make vertical alignment film, but it requires the processes of thermal annealing and ultraviolet (UV) light irradiation [7]. Lackner and Margerum [8] also reported the vertical alignment of LC with self-assembled siloxane monolayers, which requires the complex fabrication procedure of vacuum deposition.

Following on from their work, this paper reports a new vertical alignment method with a self-assembled monolayer (SAM) film. The film was based on the electrostatic adsorption self-assembly of alkyl sulfonic salts. The formation of this SAM alignment monolayer does not need rubbing, exposure process or vacuum deposition. In addition, the LC cell with this vertical alignment film exhibited good electro-optical (E-O) properties. In further investigations, we found that the alignment behaviour of the LC was critically dependent on the length of alkyl tail in self-assembled films. Using atomic force microscope (AFM) detection, the reason for this experimental result is also discussed.

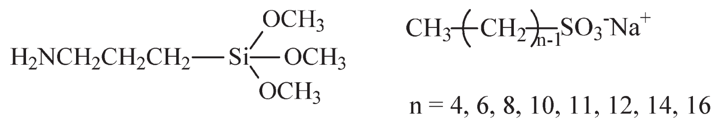
2. Experimental

2.1. *Preparation of self-assembled films*

Scheme 1 shows the chemical structures of materials used in this study. Alkyl sulfonic sodium salts and 3-aminopropyltriethoxysilane were bought from Aldrich Co. and used directly without further purification. The sulfonic sodium salt was dissolved in deionized water with a concentration of 1.0 mg ml^{-1}.

*Corresponding author. Email: yaolishuang624@163.com

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701342945



Scheme 1. Chemical structures of 3-aminopropyltriethoxysilane and sulfonic salts.

Clean quartz substrates were modified by amino groups using 3-aminopropyltriethoxysilane, via the technique proposed by Haller [9]. The amino substrate was immersed in hydrochloric acid of $1\,\mathrm{mol\,l^{-1}}$ concentration for 10 min. Then the substrate was dipped into the solution of alkyl sulfonic salt for specific time. Due to the action of electrostatic adsorption [10], the alkyl sulfonic salt was self-assembled onto the substrate.

2.2. *Surface measurement of the SAM*

The water contact angle of the film surface was measured in the process of self-assembling by a contact angle analyser (JJC-I., Changchun No.5 Optical Instrument Co., China). The contact angles along the four directions every 90° at horizontal direction were measured and averaged as the result. The topography of the film was detected with AFM method (Dimension 3100s, Digital Instrument Co., USA.).

2.3. *LC alignment behaviors*

Liquid crystal (LC) cells were fabricated as sandwich type with two substrates coated by self-assembled films, and the thickness was 4 µm. The nematic LC MJ98468 (negative-type, Merck) and 5CB (positive-type, Slichem Co., China.) were injected to the LC cells for E-O and alignment property tests. The alignment behaviour of the LC was evaluated using a polarized microscope (BX-51, Olympus) with crossed polarizers.

The polarized IR absorption spectrum of the LC cell was determined to analyse the LC alignment direction using FTIR spectrometry (FTS-3000, BIO-RAD, USA). The E-O characteristic was measured with an LCD parameters tester (LCT-5016c, Changchun Liancheng Instrument Co. Ltd.).

3. Results and discussions

3.1. *Formation of the self-assembled film*

In this work, self-assembled monolayer film was prepared through an electrostatic chemical reaction on the surface of quartz substrate. The reaction route is illustrated in figure 1. Firstly, the surface of substrate was modified with amino group by treatment of 3-aminopropytriethoxysilane; the structure of the resulting surface is illustrated in figure 1a. When the substrate with amino group was immersed in the solution of hydrochloric acid, the surface was converted to ammonium cations (figure 1b). When the treated substrate was dipped into a solution of alkyl sulfonic sodium salt, alkyl sulfonic groups would react with the substrate decorated with ammonium cations by an electrostatic adsorption reaction; hence, a self-assembled monolayer film was obtained (figure 1c). Self-assembled films with variant alkyl chains [$CH_3(CH_2)_{n\text{-}1}SO_3Na$, n=4, 6, 8, 10, 11, 12, 14 and 16] were prepared, hereafter referred to as C*n*-SAM.

During the process indicated by figures 1b and 1c, the water contact angle of the film was used to detect the self-assembled reaction. Figure 2 plots the contact angles of C11-SAM as a function of the adsorption time. The contact angle of the SAM clearly rises with an increase of reaction time, which indicates that formation of alkyl structures enhanced the hydrophobic nature of the surface. After about 10 s, the contact angle of SAM was saturated, indicating that the self-assembled reaction of the substrate was completed. It suggests that the electrostatic adsorption reaction is fast. Hence, the deposition time was chosen as 60 s for preparation of the C*n*-SAM films.

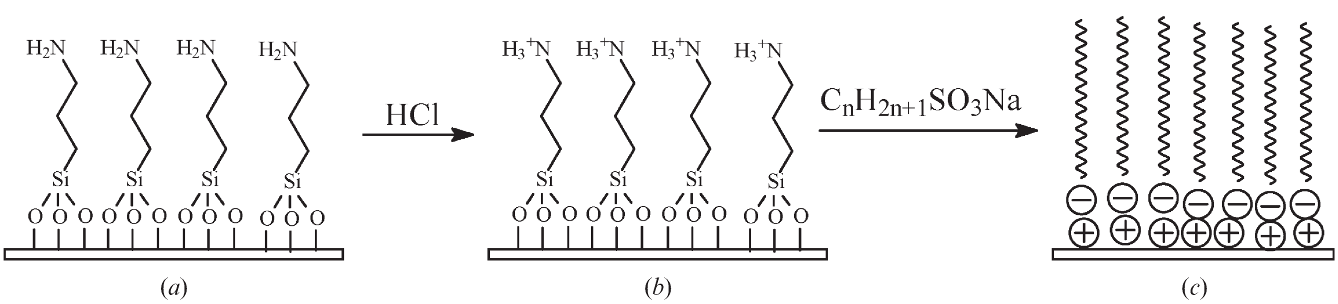


Figure 1. Illustration of the chemical structure transform of the substrate surface.

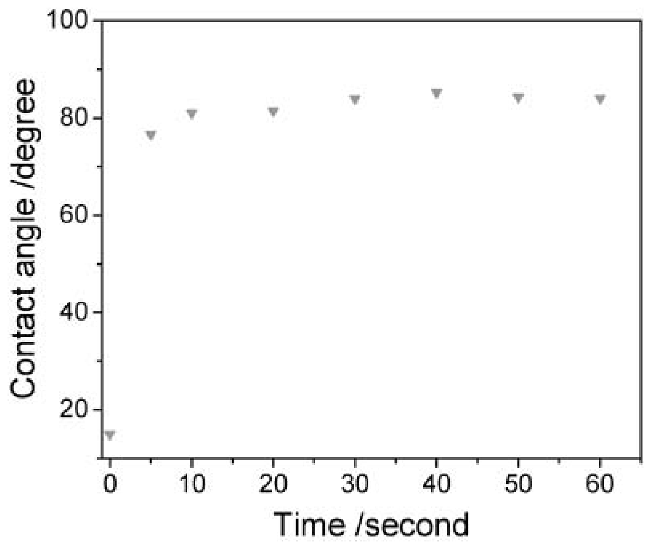


Figure 2. Contact angles of C11-SAM film as a function of deposition time.

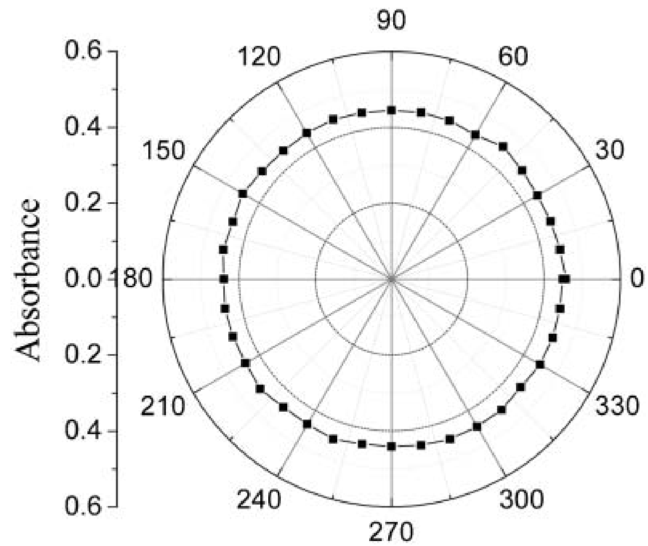


Figure 4. Polar absorbance of LC cell with C11-SAM film depending on detection angle.

3.2. *LC alignment behaviours*

The alignment behaviour of C11-SAM film was firstly evaluated via the polarized microscopy method. An obviously dark state, shown in figure 3, was found in field of vision, though the object stage was rotated. In the conoscope mode of the polarized microscope, a dark crossed brush appeared, as shown in the inset to figure 3. It shows that a vertical alignment of LC was obtained in the LC cell with C11-SAM film.

In order to further detect the alignment direction, polarized IR spectra of 5CB in the LC cell were measured. Figure 4 shows the polar coordinates diagram of IR absorbance at 2231 cm^{-1} of LC (5CB) molecules in the device. As shown in figure 4, the absorbance in the horizontal direction of all the LC molecules in this tested LC cell is the same, indicating that the alignment of LC on C11-SAM film is not a planar parallel alignment. All these results confirmed that most of the LC molecules were aligned perpendicularly to the substrate surface [11].

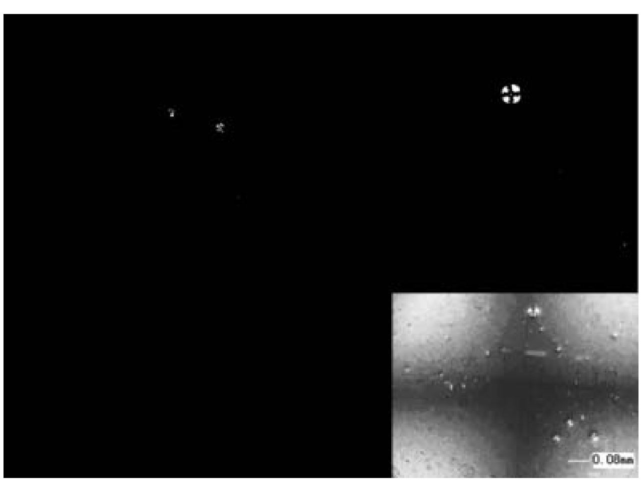


Figure 3. Optical micrographs of the homeotropic alignment of LC cell with C11-SAM film under crossed polarizers mode and under crossed polarizers mode with conoscope (inset).

Moreover, serial SAM films with *n* values of 4, 6, 8, 10, 11, 12, 14 and 16 were used as alignment film; the alignment results are systematically summarized in table 1. It is revealed that C11-SAM is a critical point; only when the value of *n* approaches 11 or larger, could a fine homeotropic alignment be obtained; otherwise the alignment property was disordered.

To investigate the reason why SAM films with different alkyl chain length showed different alignment properties, the surface morphology of the SAM film was characterized by AFM method. Figure 5 shows the AFM images of C10-SAM film and C11-SAM film, respectively. It was shown that the morphology of C10-SAM is rather smooth with an rms (root-mean-square

Table 1. Statistics of the alignment properties of LC on different SAM films.

Length of alkyl chain	Alignment behaviour	Quality of alignment
<11	disordered	N/A
11	vertical	uniform
12	vertical	uniform
14	vertical	uniform
16	vertical	uniform

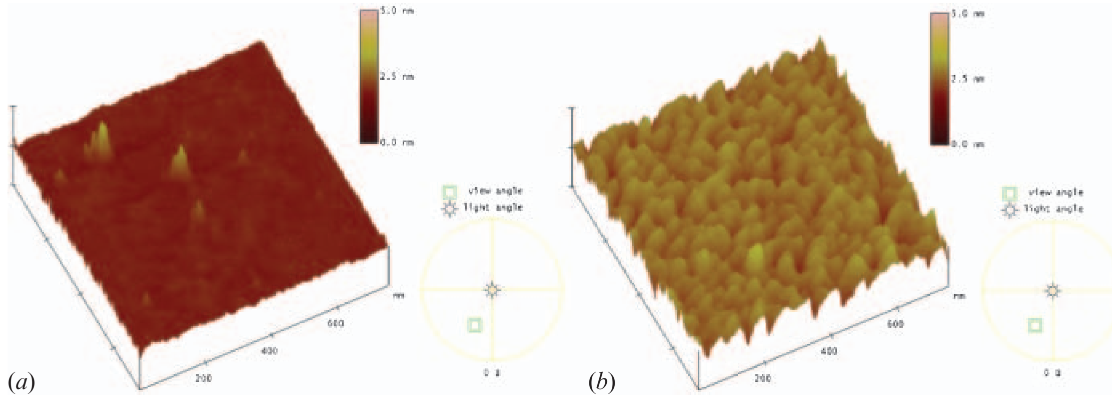


Figure 5. AFM images of (a) C10-SAM films and (b) C11-SAM.

roughness) value of 0.292 nm, which is as small as the clean substrate. However, the rms value of C11-SAM film is high, up to 0.671 nm, nearly three times as large as that of C10-SAM. Hence, it was concluded that the surface with relative rough topography could induce the homeotropic alignment of LC. These results are in good agreement with Nakagawa's research [12] about construction of SAM. In the formation of SAM, when the alkyl chain length was larger than a specific value, an ordered self-assembled film is formed by the Van der Waals force between each alkyl chain, and the alkyl chain is mainly vertical to the substrate. On the other hand, when the alkyl chain length is too short, the substrate adsorbed the alkyl chain in a disordered state because of the weak Van der Waals force, and most of alkyl chains would be parallel to substrate; the rms value would be less than that of the SAM with alkyl chain in vertical state. Therefore, the roughness of C11-SAM is larger than that of C10-SAM.

3.3. *E-O characteristics*

Figure 6 compares the transmission voltage characteristics of VA-mode LC cells with C11-SAM and commercial homeotropic PI film (JALS-2021-R1, Japan Synthetic Rubber Co.). The cells were fabricated with 4 μm gaps and injected with negative-type LC, and the polarizing direction of polarizer and analyser was perpendicular in the LCD tester. Two similar E-O curves were obtained, showing good *V-T* property and high contrast ratio. Moreover, a low threshold voltage of 3 V on SAM film compared to the high threshold voltage of about 10 V on PI film is revealed, which probably shows the relatively weak anchoring effect of SAM alignment film. All the results confirmed that a fine vertical alignment of LC on C11-SAM film is achieved.

3.4. *Thermal stability of the alignment film*

Thermal stability is another important factor for vertical alignment films. We evaluated the thermal stability of the SAM film by an annealing method. At different temperature, the LC cell contained 5CB was heated for 30 min and then cooled down to room temperature naturally. It was found that after annealing the LC cell with C11-SAM film exhibited a uniform dark state under polarized microscopy until 270°C. Figure 7 shows the pretilt angle of LC cell with C11-SAM at different annealing temperatures, and the value of the pretilt angle was between 89° and 90°, which meant that the SAM alignment film could maintain vertical alignment state at high temperature. This thermal stability of C11-SAM film is comparable with conventional PI alignment film, which must be attributed to the stable electrovalent linkage between substrate and alkyl chain. In more experiments, it was

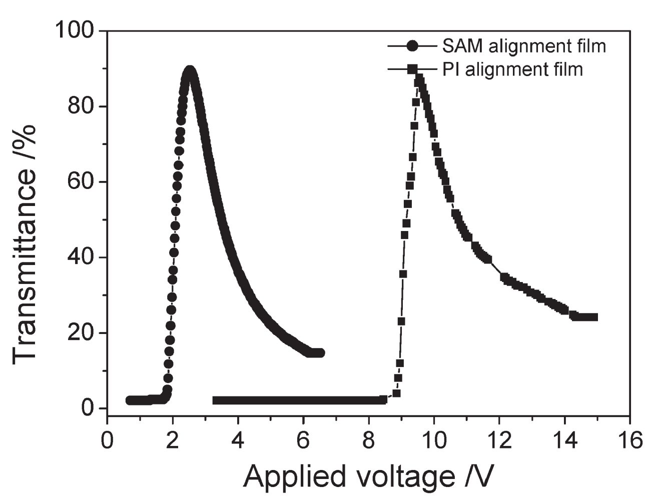


Figure 6. The voltage dependent transmittance curve for LC cells with C11-SAM film and rubbed homeotropic PI film.

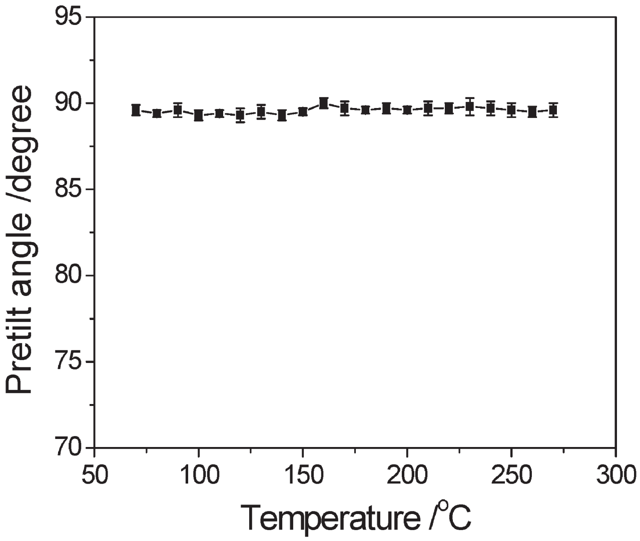


Figure 7. The pretilt angle of the vertical alignment film of C11-SAM at different process temperatures.

proved that the alignment films of C12, C14, C16-SAM all could provide good thermal stability to 270°C.

4. Conclusions

A vertical alignment film based on the electrostatic self-assembly of sulfonic salt was investigated without rubbing and UV exposure. With tests using polarized microscopy and polarized IR absorption spectrometry, the vertical alignment of LC was demonstrated. Furthermore, it is found that only when the number of carbon atoms in the alkyl chain of sulfonic salt is 11 or larger, vertical alignment is achieved; otherwise the result is a poor alignment of LC. By the detection of the morphology of the SAM films, we conclude that the rough surface of SAM film with certain length of alkyl chain determines the vertical alignment of the LC. Moreover, the vertical alignment film for nematic LC exhibits fine E-O properties and an excellent thermal stability.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (Grant No. 50473040, 60578035) and the Natural Foundation of Jilin Province (Grant No. 20050520, No.20050321-2) for financial support.

References

[1] T. Geelhaar. *Liq. Cryst.*, **24**, 91 (1998).
[2] M. Schadt, W. Helfrich. *Appl. Phys. Lett.*, **18**, 127 (1971).
[3] M. Oh-e, K. Kondo. *Appl. Phys. Lett.*, **67**, 3895 (1995).
[4] M.F. Schiekel, K. Fahrenschon. *Appl. Phys. Lett.*, **19**, 391 (1971).
[5] C. Chen, P.J. Bos, J. Kim. *J. Appl. Phys.*, **99**, 23523 (2006).
[6] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki. *Langmuir*, **4**, 1214 (1988).
[7] H.F. Li, E.J. Kim, H. Furue. *Mol. Cryst. Liq. Cryst.*, **326**, 249 (1999).
[8] A.M. Lackner, J.D. Margerum, L.J. Miller. "Photostable Tilted-Perpendicular Alignment of Liquid Crystals for light values", *Society for Information Display International Symposium Digest of Technical Papers*, **XXI**, pp. 98–101 (1990).
[9] I. Haller. *J. Am. Chem. Soc.*, **100**, 8050 (1978).
[10] T.S. Lee, J. Kim, J. Kumar. *Macromol. Chem. Phys.*, **199**, 1445 (1998).
[11] K. Ha, H.J. Ahn, C. Son. *Liq. Cryst.*, **33**, 935 (2006).
[12] T. Nakagawa, M. Soga. *Jap. J. Appl. Phys.*, **36**, 6915 (1997).