

## STUDY ON PHOTO-INDUCED ORIENTATION OF A NOVEL PHOTO-ALIGNMENT FILM WITH SURFACE ENHANCED RAMAN SCATTERING (SERS) SPECTROSCOPY\*

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**Abstract** Surface enhanced Raman scattering (SERS) spectroscopy was first utilized to study the photo-orientation behaviour of the photoreactive groups on a novel photo-alignment film surface and elucidate the generation mechanism of pretilt angle. The novel photo-alignment film was prepared by spin-coating a solution of ladderlike polysiloxane (LPS) bearing dual photoreactive group on an ITO surface and by irradiation with linear-polarized ultraviolet (LPUV) light. A Si—H terminal compound (M) containing an identical photosensitive part has been used to fabricate a model film for SERS investigation.

**Keywords** Alignment film, Photo-induced orientation, Surface enhanced Raman scattering (SERS), Pretilt angle

### INTRODUCTION

The control of the orientation of liquid crystalline molecules is essential for high-performance liquid crystal displays (LCD), which is commercially achieved by mechanically rubbed polyimide film coated on indium tin-oxide (ITO) glass substrate. A decade ago, the photo-alignment technique, as a promising non-contact technique and an alternative to the conventional rubbing process, was invented in order to avoid the shortcomings of the rubbing technique<sup>[1]</sup>. However, the mechanism of photo-induced alignment of the molecules on the surface and of generation of pretilt angle still has not been clearly explained. Some surface-sensitive measurements including photoelectron spectroscopy for chemical analysis (ESCA), AFM for topological study, X-ray scattering, surface optical second harmonic generation (SHG) and SERS have been utilized to investigate the molecular orientation and conformational change on the rubbed polyimide surface<sup>[2–4]</sup>. Among them, SERS is now considered as one of the prominent techniques in the area of surface characterization. In this study, we first utilize the SERS method to study the conformation changes of a novel photo-alignment film surface in order to further discover the mechanism responsible for the photo-induced alignment and generation of pretilt angle ( $\theta$ ).

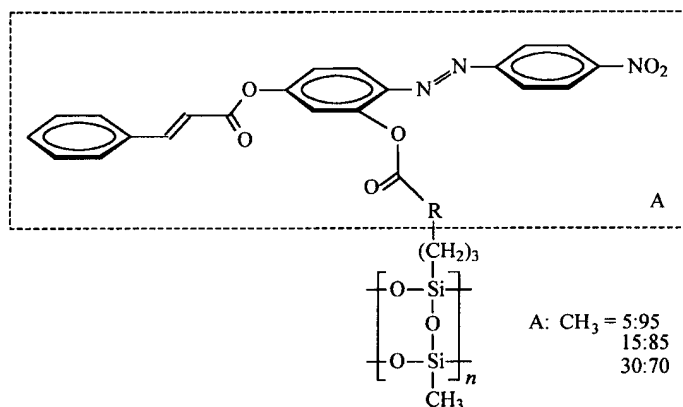
As an inorganic/organic hybrid, the ladder-like polysilsesquioxanes (LPSs) possess many excellent properties, such as colorless and transparent appearance, glasslike film-forming ability, good adhesion to glass and silicon-chip and superior solubility in common organic solvents, and they have potentially ideal skeleton materials for photo-alignment applications<sup>[5]</sup>. Accordingly, a novel series of LPS containing dual photo-reactive

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side chains grafted in side-on manner and with various ratios was synthesized as shown in Scheme 1. We anticipate that both photo-orientation and photo-crosslinking of the neighboring dual moieties groups, cinnamoyl and *p*-nitroazobenzene, would take place concertedly after proper irradiation and result in better alignment stability.



**Scheme 1** Schematic molecular structure of LPS-CA ( $R = (CH_2)_{10}Si(CH_3)_2OSi(CH_3)_2$ ), monomer (M) = A

## EXPERIMENTAL

The procedures for the synthesis of monomer (M) and the polymer (LPS-CA) can be found in a previous report<sup>[6]</sup>. Both spin-coated M and LPS-CA films were vertically irradiated with LPUV light (300–365 nm) followed by annealing treatment. The UV exposure system consists of a 500 W Hg lamp, a quartz convex lens and a Glan-Taylor polarizing prism. FT-Raman experiments were run using a Bruker IFS 100 FT-Raman Spectrometer. The SERS-active substrates involved a silver colloidal deposition method via the reduction reaction of  $AgNO_3$ <sup>[7]</sup>. A  $13 \times 26$  mm piece of irradiated substrate modified with M film was placed in a 10 mL beaker and 3 mL silver ammonia complex and 2 mL glucose were mixed in the beaker. After 3–5 min, the solution became gray and black. The silver ions were reduced to form colloidal particles and were deposited onto the film surface at room temperature. The film covered with silver over-coating was dried under an infrared lamp.

A test LC cell (5  $\mu$ m thick LC layer) was sandwiched with the photo-alignment film covered ITO glasses and filled with nematic LC (5CB,  $T_{NI} = 35^\circ C$ ) at  $50^\circ C$ . The cell was then annealed at  $50^\circ C$  for 15–20 min. The  $\theta$  values were measured by the crystal rotation method<sup>[8]</sup>.

## RESULTS AND DISCUSSION

### Characterization of the Photo-alignment Effect in a LC Cell

In principle, photo-alignment materials can be primarily divided into two categories based on the type of functional groups employed. The first category is capable of undergoing photo-induced isomerization from *trans* isomer (*E*-isomer) to *cis* isomer (*Z*-isomer) and *vice versa*, such as azobenzene-containing polymers<sup>[1]</sup> and the second category consists of polymers that can be anisotropically photo-crosslinked on illumination with LPUV light, *e.g.*, polymers containing cinnamoyl or coumarin groups<sup>[9, 10]</sup>. The molecular design in this report, dealing with a dual photoreactive group consisting of photo-crosslinkable cinnamoyl and photo-isomerizable *p*-nitroazobenzene, was intended to have homogeneous alignment quality, as well as higher pretilt angles as a result of concerted photoreactions. The molded M film was prepared by condensation reaction of terminal Si–H with hydroxy-groups on the glass surface.

LPSs grafted with photoreactive side chains in 5%, 15%, and 30% molar ratio were prepared as shown in Scheme 1. It was found that the film spin-coated with the 30% one (LPS-CA30) could attain the best alignment effect, which may result from higher density of photoreactive groups grafted. Grafting ratios higher than 50%,

however, could not be achieved because of the expected large volume occupation of side groups. Therefore, the following characterizations were all performed with LPS-CA30.

As expected, the LC cell assembled with the LPS-CA30 or M coated substrates exhibits a homogeneous alignment (almost mono-domain) with adjustable tilt angles ( $\theta = 2^\circ - 7^\circ$ ) by varying the UV-light intensity ( $2 - 5 \text{ mW/cm}^2$ ). The macroscopic orientation behavior of the LC cell was observed by using a polarizing optical microscope (POM). It was noted that annealing treatment at  $50^\circ\text{C}$  for 15–20 min before and after illumination can markedly improve the alignment quality. A few defects on the image (Fig. 1a) were self-healed after annealing or just laying aside overnight and the  $\theta$  values were raised by  $2 - 3^\circ$  (Figs. 1b and 1c). The thermally enhanced photo-alignment in this case may be attributed to the raising mobility of the groups on the film surface<sup>[9e]</sup> and the command effect of the photo-induced oriented chromophores on the non-reacted groups<sup>[11]</sup>. Also, annealing treatment lowered the viscosity of the LC layer which was helpful for bulky LC molecules to transfer the surface anchoring effect and to align more uniformly. The periodical azimuthal angular dependent changes of light transmittance through two crossed polarizers are also shown in Fig. 1(d).

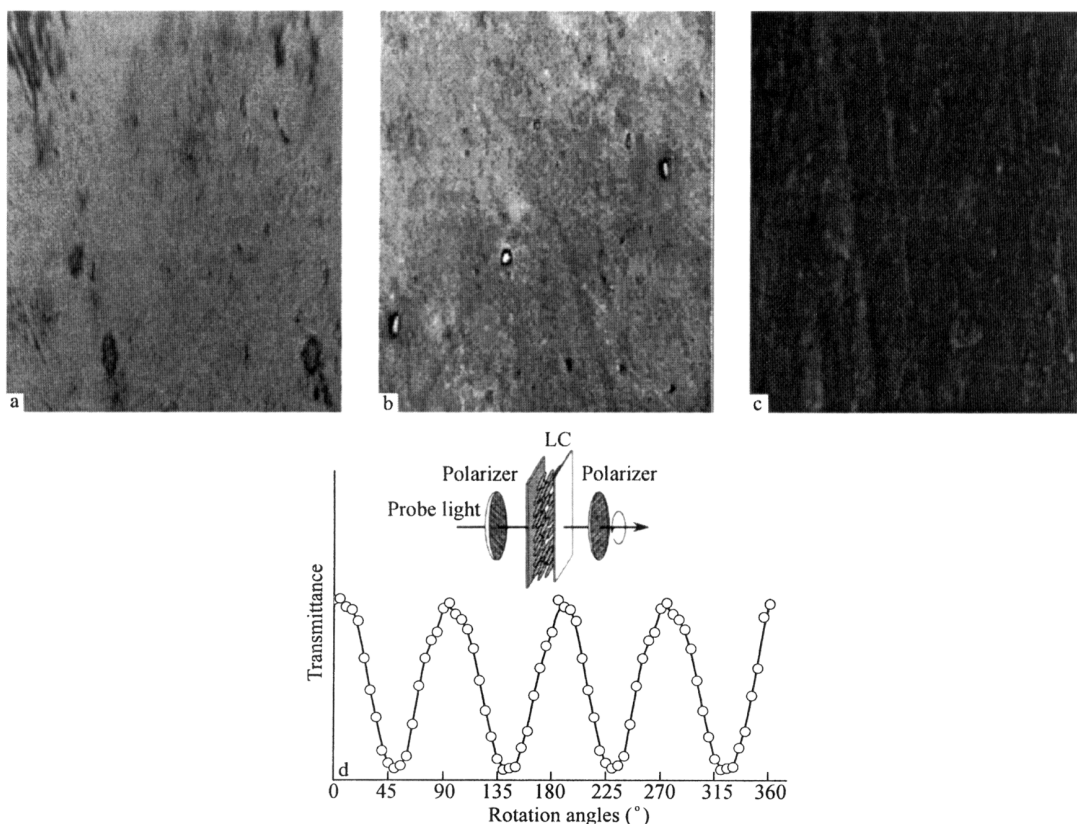
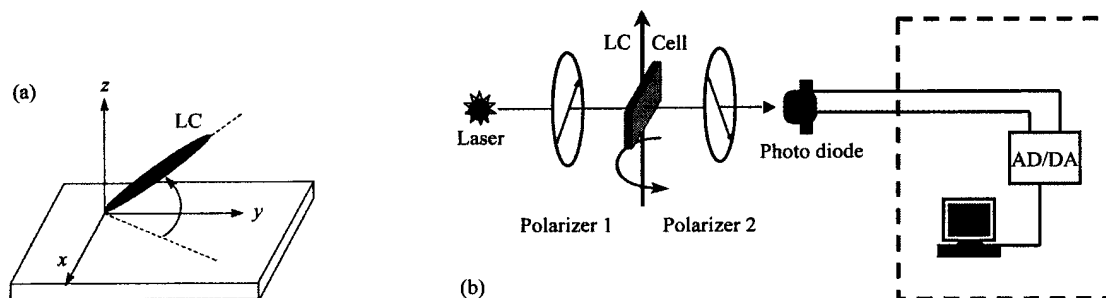


**Fig. 1** Polarizing optical microscopic images of LC cell irradiated by LPUV light of  $5.55 \text{ mW/cm}^2$  intensity  
a) With some defects, before annealing; b) Under bright field; c) Under dark field after annealing;  
d) Angular dependent light transmittancy through two crossed polarizers of the same LC cell

For practical LCDs, pretilt angle ( $\theta$ ) of LC molecules on the alignment film, defined as the angle between its director and substrate plane, as illustrated in Scheme 2(a), is a key factor influencing the response speed and display quality. Advanced super-twisted nematic (STN) mode LCDs demand higher pretilt angles of  $5^\circ - 10^\circ$ . Normally,  $\theta$  is measured by the crystal rotation method as shown in Scheme 2(b). The  $\theta$  value up to  $7^\circ$  of our test cells was determined by the optimized irradiation and annealing treatment.



**Scheme 2.** a) Illustration of pretilt angle and b) setting for measuring pretilt angles by the crystal rotation method

In order to morphologically gain a deep insight into the mechanism of photo-alignment and the pretilt generation at the molecular level, SERS measurements were performed as follows.

#### **Study on the Photo-Alignment Film Surface with SERS Spectroscopy**

According to the surface selection rule of SERS for molecules adsorbed on a metal surface, the signals of molecular vibrations with moments perpendicular to the substrate surface are intensified, while those with moments parallel to the surface are weakened. This rule makes SERS uniquely surface-specific and capable of detecting the chain conformation and orientation at the surface. To avoid overlaying the absorption of the chromophores with the strong absorptions of LPS itself in the Raman spectrum region, the monomer (M) with reactive Si—H terminal group, as model compound, which contains an identical photosensitive part and exhibited the same alignment behavior as M-grafted polymer (LPS-CA), was chosen for SERS measurements.

Normal FT-Raman spectrum of the bulk sample and SERS spectrum of M film before irradiation were recorded as shown in Figs. 2(a) and 2(b). Comparison between Figs. 2(a) and 2(b) reveals that the disappearance of the CH<sub>2</sub> deformation vibration, the C—Si stretching vibration, the C—C stretching vibration of aliphatic chain and the Si—O—Si asymmetric stretching vibration (1459 cm<sup>-1</sup>, 1239 cm<sup>-1</sup>, 1149 cm<sup>-1</sup> and 1103 cm<sup>-1</sup>, respectively) along with the enhancement of the CH<sub>2</sub> symmetric and asymmetric stretching vibration (2834 cm<sup>-1</sup> and 2914 cm<sup>-1</sup>) indicate that the long aliphatic chains tend to lie more parallel to the film surface. Meanwhile, the marked enhancement of the N=N stretching, the NO<sub>2</sub> symmetric stretching, the C—N (NO<sub>2</sub>) stretching, the symmetric C—O—C stretching of ester group (which links the aliphatic chain and the azobenzene) and the 1,2,4-C<sub>6</sub>H<sub>3</sub> benzene ring C—H deformation vibration (out-of-plane) (the last one may also involve NO<sub>2</sub> deformation vibration) (1413 cm<sup>-1</sup>, 1335 cm<sup>-1</sup>, 891 cm<sup>-1</sup>, 919 cm<sup>-1</sup> and 687 cm<sup>-1</sup>) suggest that the transition moment of the *p*-nitroazobenzene adopts an out-of-plane conformation on the spin-cast film surface before irradiation.

The difference spectrum between Figs. 3(a) and 3(b) (before and after irradiation) is given in Fig. 3(c). The significantly enhanced signals of the following vibration modes at 1413 cm<sup>-1</sup>, 1335 cm<sup>-1</sup>, 891 cm<sup>-1</sup>, corresponding to the N=N stretching, the NO<sub>2</sub> symmetric stretching and the C—N (NO<sub>2</sub>) stretching vibrations respectively, indicate that the *p*-nitroazobenzene moieties assume a more tilted out-of-plane conformation after irradiation. The polar angle between the transition moment of the *p*-nitroazobenzene moiety and the surface increases after irradiation and it must play an essential role in generating a high pretilt angle. Moreover, the enhancement of the peak at 687 cm<sup>-1</sup> associated with the 1,2,4-C<sub>6</sub>H<sub>3</sub> benzene ring C—H deformation vibration (out-of-plane) and the obvious decrease of the peak at 919 cm<sup>-1</sup> associated with symmetric C—O—C stretching vibration of the ester (which links the aliphatic chain and the azobenzene) must be related to the tilting up of the *p*-nitroazobenzene group. Consequently, the significant tilting-up of the *p*-nitroazobenzene units at the uppermost surface of photo-alignment film, which leads to the generation of higher  $\theta$ , is further confirmed by the SERS results.

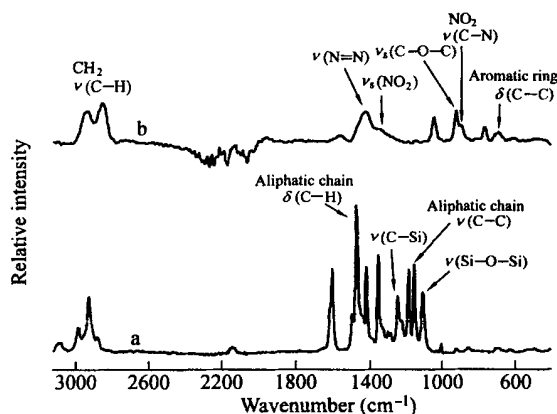


Fig. 2 a) FT-Raman spectrum of the bulk sample of M; b) SERS spectra of M-thin film before irradiation

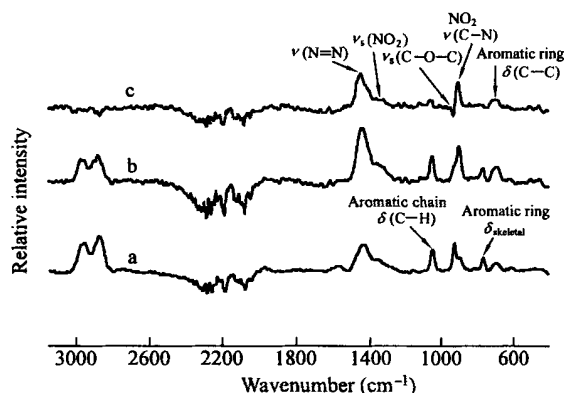


Fig. 3 SERS spectra of M-thin film  
a) Before irradiation;  
b) After irradiation;  
c) Difference spectrum between a) and b)

## CONCLUSIONS

A novel series of LPSs containing dual photoreactive groups (*p*-nitroazobenzene and cinnamoyl), in the side-on mode, has been synthesized. Among them, LPS-CA30 has been successfully utilized to fabricate photo-alignment layers, which can induce homogeneous alignment of LC molecules with adjustable pretilt angles ( $\theta$ ) (2–7°). The mechanism of the photo-induced orientation and the generation of high  $\theta$  have been elucidated for the first time by SERS measurements. The results indicate that the concerted photoreactions may be responsible for generating uniform homogeneous photo-alignment and the isomerization and spatial reorientation of the *p*-nitroazobenzene groups must result in the higher  $\theta$ .

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