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Photo-Induced Orientation of a Film of Ladderlike Polysiloxane Bearing Dual Photoreactive Side Groups**

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The control of the orientation of liquid crystalline molecules is essential in liquid crystal displays (LCDs), and is usually achieved by coating an alignment film on the conductive ITO (indium tin oxide) glass surface. The photo-alignment (PA) technique as one promising alternative to the widely used conventional rubbing process of a polyimide (PI) substrate has been studied extensively in the last decade, because it provides a simple and non-contact fabrication process suitable for advanced thin film transistor (TFT) LCDs. In principle, the PA materials can be primarily divided into two categories based on the type of functional groups employed. The first ones are capable of undergoing photo-induced isomerization from trans isomer (*E*-isomer) to *cis*-isomer (*Z*-isomer) and vice versa; this category includes molecules such as azobenzene-containing polymers.[1] The second category consists of polymers that can be anisotropically photo-cross-linked on illumination with linear polarized ultraviolet (LPUV) light; this includes examples such as polymers containing cinnamoyl or coumarin groups.[2,3] In particular, Schadt,[2b–d] and O'Neill and Kelly[4] recently demonstrated that the films based on coumarin exhibit high sensitivities and high pretilt angles (up to 7.5°), although the alignment was ascribed to unstable photo-degradation rather than cross-linking. However, despite the promising future of the PA technique, the search for materials possessing fine comprehensive performance still remains a great challenge.

As an inorganic–organic hybrid, the ladder-like polysilsesquioxanes (LPSs) possess many excellent properties, such as being colorless and transparent, glasslike film-forming ability, high adhesion to glass and silicon chips, and superior solubility in common organic solvents, and are potentially ideal skeleton materials for PA applications.[5,6] Accordingly, a novel LPS containing dual photo-reactive groups, cinnamoyl and *p*-nitroazobenzene, attached in a side-on fashion, was synthesized (Scheme 1, which also shows the structure of the final polymer). The molecular design was based on the following considerations:

- the azobenzene-containing polymer films often have a higher degree of tilted orientation and photosensitivity than the photo-cross-linking ones;[7]
- the threshold dose required to obtain a superior alignment for the side-on azo-grafted polymer is substantially smaller than that of the end-on ones;[8]
- both the photo-orientation and photo-cross-linking of the neighboring dual moieties would take place collaboratively after proper irradiation and most likely result in better alignment stability.

As expected, the LC cell assembled using the LPS-CA30 coated substrates exhibits a uniformly homogeneous alignment (almost mono-domain) with a long temporal stability (over one year at room temperature) and an adjustable tilt angle ($\theta = 1\sim7°$) by variance in UV-light intensity ($2\sim 5$ mW cm^{-2}). The macroscopic orientation behavior of the LC cell was observed by polarizing optical microscopy (POM). It was noted that annealing after illumination markedly improved the alignment quality. A few silk-like defects on the dark-field image were self-healed after annealing or just leaving overnight, and the θ values increased by 2~3°.

In order to morphologically gain a deep insight into the mechanism of PA and the pretilt generation at the molecular level, the photo-induced dichroism difference ($\Delta A = A_{\parallel} - A_{\perp}$) of the LPS-CA30-based PA film was examined by a polarized UV spectrometer. As shown in Figure 1, both the absorbance of the azobenzene group ($\lambda_{\max} = 375$ nm) and of the cinnamoyl group ($\lambda_{\max} = 255$ nm) show negative dichroism ($\Delta A < 0$) simultaneously, implying that the photoreactions of the dual photo-reactive groups jointly participate in the generation of azimuthal anisotropy of the film; the in-plane absorbencies of both $A_{\parallel}$ and $A_{\perp}$ of the azobenzene group are reduced concurrently after irradiation, suggesting that the *E*–*Z*–*E* isomerization of the azobenzene groups leads primarily to an out-of-plane (spatial) reorientation. Remarkably, this PA film with dual photoreactive groups induces a homogeneous alignment

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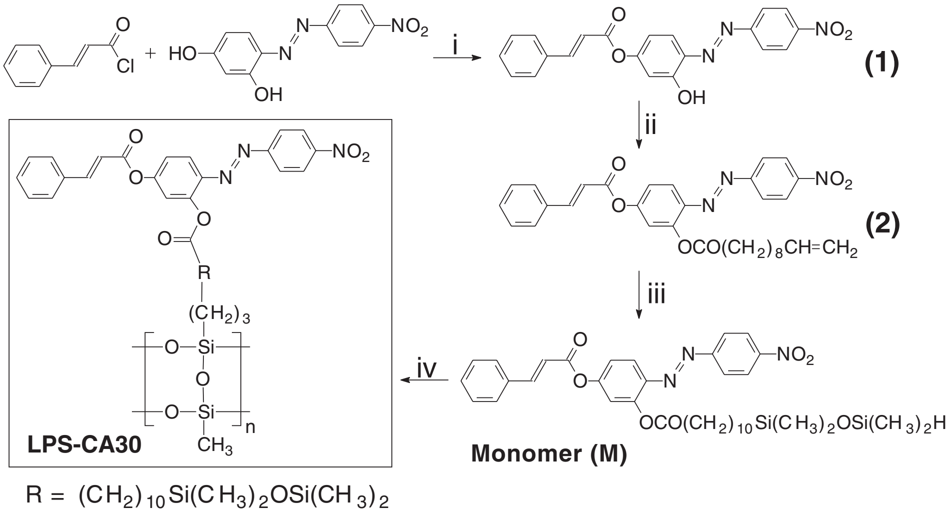

Scheme 1. Synthesis of the novel LPS containing dual photo-reactive groups, cinnamoyl and *p*-nitroazobenzene, attached in a side-on fashion.

with a much higher θ than the corresponding exclusive cinnamoyl-containing ones by vertical irradiation.[2a,b,9]

Surface-enhanced Raman scattering (SERS), as a surface-specific technique, was first successfully introduced by Cheng and co-workers to study the essence of rubbing on the PI surface morphology recently.[10] Thus, we explore this powerful tool to provide a morphological understanding of spatial reorientation and conformational changes of the azobenzene groups at the uppermost surface after irradiation. To avoid overlaying the absorption of the chromophores with the strong absorptions of LPS itself in the Raman spectrum region, the monomer (M), as model compound, which comprises identical photosensitive parts and exhibits the same alignment behavior as LPS-CA30, was chosen.

As compared with the bulk Fourier transform Raman spectrum (Fig. 2a), the SERS signals (Fig. 2b) at 1413 cm^{-1}, 1335 cm^{-1}, 891 cm^{-1}, 919 cm^{-1}, and 687 cm^{-1} of the *p*-nitroazobenzene vibrations reveal marked enhancement, suggesting that its transition moment takes on an out-of-plane conformation before irradiation (Fig. 3a). According to the difference spectrum (Fig. 2d), the significant enhancement of the signals at 1413 cm^{-1}, 1335 cm^{-1}, 891 cm^{-1}, and 687 cm^{-1}, and the noticeable decrease at 919 cm^{-1} (symmetric C–O–C stretching of ester group linking the aliphatic chain and the azobenzene) indicate that the *p*-nitroazobenzene moieties adopt 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 (Fig. 3a). Consequently, the significant tilting-up of the *p*-nitroazobenzene units at the uppermost PA surface, which leads to the generation of higher θ, is further confirmed by the SERS results.

In addition, a great decrease in the intensity of the –C=C– vibration at 1600 cm^{-1} of the cinnamoyl groups was noticed in the FTIR spectrum of the irradiated film, which supports the fact that majority of the cinnamoyl groups do undergo cycloaddition reaction rather than isomerization. As clearly pointed out by Reiser and co-workers,[11] the "head-to-head"

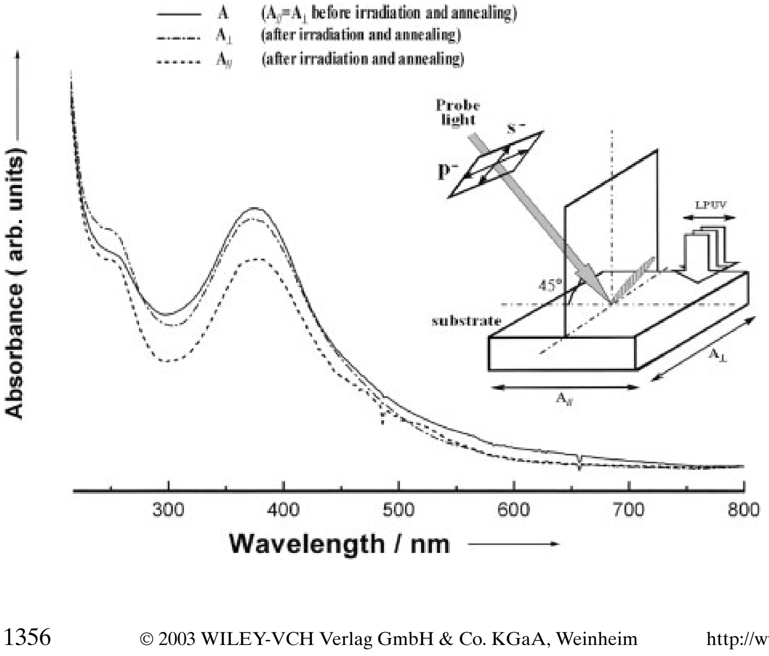

Fig. 1. Polarized UV-vis absorption spectra of the LPS-CA30 film before and after vertical irradiation and subsequent annealing; $A_\parallel$ and $A_\perp$ represent the absorbance parallel and perpendicular to electric vector (E) of the irradiating LPUV light, respectively.

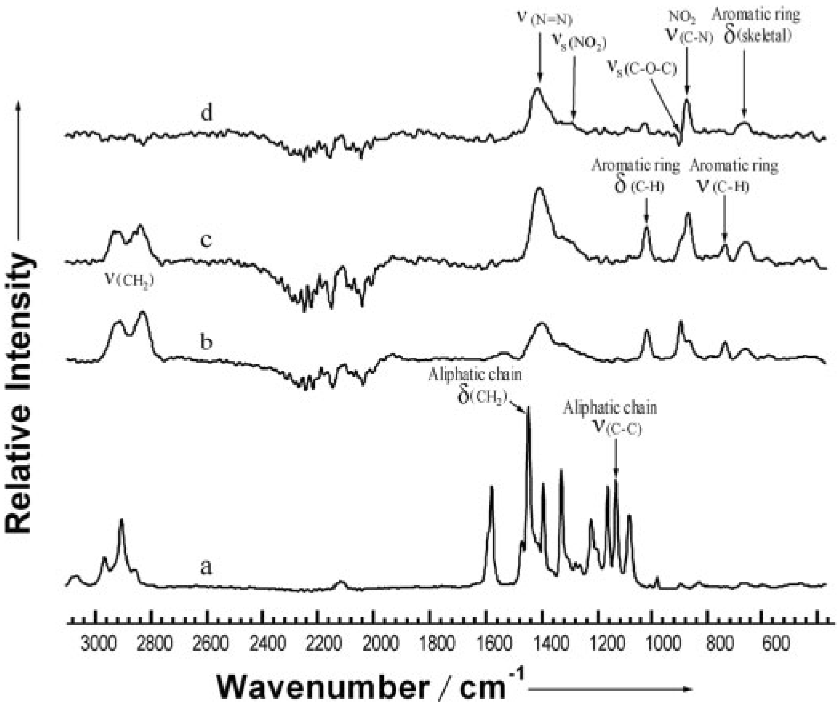

Fig. 2. FT-Raman spectra of a) the bulk sample of M; b,c) SERS spectra of M thin film before irradiation (b) and after irradiation (c); d) difference spectrum between (b) and (c).

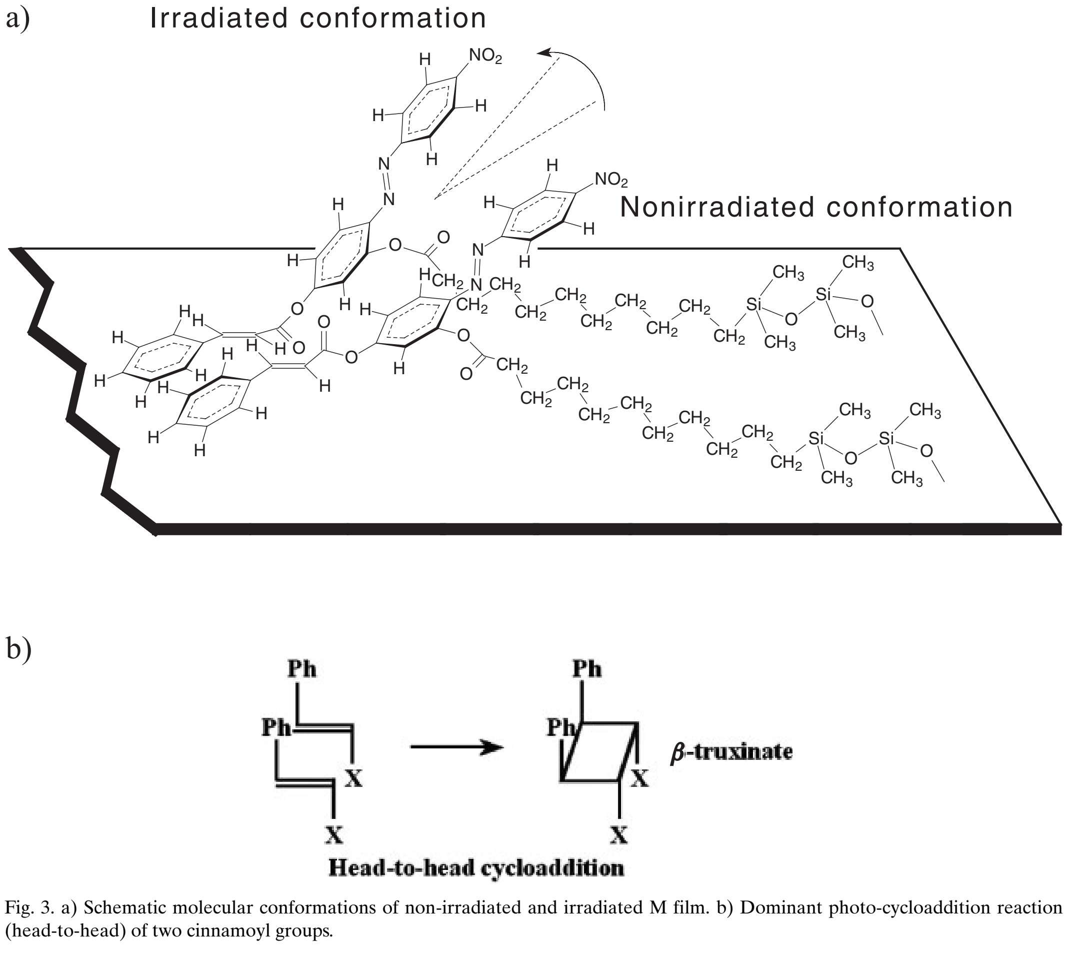

Fig. 3. a) Schematic molecular conformations of non-irradiated and irradiated M film. b) Dominant photo-cycloaddition reaction (head-to-head) of two cinnamoyl groups.

cycloaddition isomer of cinnamoyl groups, β-truxinate (Fig. 3b), is the dominant photoproduct. Interestingly, the concerted photoreactions of this very photo-cycloaddition and above-mentioned *E–Z–E* isomerization can not only cause the uniform tilting-up of *p*-nitroazobenzene moieties on the uppermost surface resulting in homogeneous PA films with higher θ value (Fig. 3a), but also stabilize the alignment through the fixing of the oriented side chains.[11]

In summary, a novel LPS containing dual photoreactive groups (*p*-nitroazobenzene and cinnamoyl) in a side-on fashion, has been synthesized and successfully utilized to fabricate PA layers that can induce homogeneous alignment of LC molecules with controllable pretilt angle ($\theta = 1°\sim7°$). The mechanism of the photo-induced orientation and the generation of a high θ value have been elucidated for the first time by a combination of inter-confirmed spectroscopic methods, including UV-dichroism, SERS, and FTIR. The results indicate that the concerted photoreactions, the isomerization and spatial reorientation of the *p*-nitroazobenzene groups, and the head-to-head photo-cycloaddition of the cinnamoyl groups, are mainly responsible for generating uniform homogenous PA with adjustable θ; the photo-cross-linking of the cinnamoyl groups is the predominant factor for the stability of the anisotropic orientation. In addition, the side-on grafting is found to be advantageous on vertical irradiation for increasing the photoreaction efficiency.

Experimental

The synthesis of LPS-CA30 was reported previously [12]. The spin-coated LPS-CA30 film was vertically irradiated by LPUV light (~300–365 nm) followed by annealing treatment (50 °C, ~15–20 min). The UV exposure system consists of a 500 W Hg lamp, a quartz convex lens, and Glan–Taylor polarizing prisms. Polarized UV dichroism was measured on a HP8453 UV-vis spectrometer (Agilent). 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 $AgNO_3$ [10]. FTIR measurements were performed with a Bruker EQUINOX55 FTIR spectrometer.

A test LC cell (5 µm thick LC layer) was sandwiched with the PA film covered ITO glass and a blank one and filled with nematic LC (5CB, $T_{NI} = 35$ °C) at 50 °C. The cell was then annealed at 50 °C for ~15–20 min The θ values were measured by crystal rotation method [13].

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Fabrication and Controlled Magnetic Properties of Ni/ZnO Nanorod Heterostructures[**]

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One-dimensional nanorod heterostructures are potentially ideal functional components for nanoscale electronics and optoelectronics.[1–4] Semiconductor nanorod heterostructures have already exhibited tunable wavelength in light emission due to the quantum confinement effect,[5] useful for many nanoscale devices. Furthermore, the ability to fabricate nanoscale heterostructures opens up many new device applications as already proven in microscale electronics and photonics.[6–8] A prime example of the heterostructures is magnetic random-access memory which is based on a magnetic/semiconductor heterostructure that exploits both the spin and charge of the carriers.[9] The combination of the two degrees of freedom promises new functionality in memory devices, detectors, and light-emitting sources. Hence, fabrication of magnetic-material/semiconductor-nanorod heterostructures is of particular interest in nanoscale spintronics. Controlled growth of nanoscale magnetic layers on a single nanorod would enable novel physical properties such as size-dependent magnetism to be exploited, which offers the tuning of remanent magnetization and coercive fields by varying the magnetic layer thickness.[10] In this paper, we report on the fabrication of magnetic-metal/semiconductor nanorod heterostructures and the metal-layer-thickness-dependent magnetic properties due to a crossover from ferromagnetism to superparamagnetism. The ability to grow tunable magnetic-metal/semiconductor nanorod heterostructures is expected to greatly increase the versatility and

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