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A Combined Method Based on Rubbing and UV-Irradiation for Preparing Stable Alignment-Layers with High Pretilt Angles

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A novel two-step method combining rubbing and UV-irradiation based on ladderlike polysilsesquioxanes (LPS) containing cinnamate and azobenzene side chains was developed to obtain alignment layers which features a high surface pretilt angle and good stability. At the first step, a low pretilt angle of 1–3° was generated by rubbing and at the second step, an increased pretilt angle of about 11° was obtained through further UV-irradiation. The polarized optical micrograph and the conoscopic picture prove that good LC alignment state with a stable high pretilt angle can be obtained by in situ photo-crosslinking of the cinnamate side-chains through proper UV-irradiation. The high pretilt angle arises from the photo-induced tautomerization of azobenzene side chains and that is confirmed by AFM study. In particular, the annealing test near the clearing point indicates the high stability of the high pretilt state, which heralds their potential application in LCD such as producing a patterned alignment layer for improving view angle.

Keywords: Polysilsesquioxanes; alignment layer; high pretilt angle

INTRODUCTION

The pre-orientation status of liquid crystals (LCs) plays a particularly important role in the performance of the liquid crystal displays (LCDs) and this status is strongly dependent on the nature of the substrate surface$^{(1)}$. Various materials and methods were studied to obtain such a homogeneous LC alignment with a

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proper pretilt, such as the oblique evaporation of SiO films(1, 2), the rubbing treatment on polymer films of polyvinylalchohol(1), polyacrylates(3), polyvinylformal(4) and poly(ethylene-terephthalate)(5), the polyimide (PI) Langmuir-Blodgett films(6). Recently Schadt developed a rubbing-free alignment method based on the polarized UV-light induced linear photo-polymerization of polyvinyl 4-methoxy-cinnamate (LPP technique)(7–12), but a satisfied pretilt angle is required to develop.

Rubbing is a widely employed technique for LC alignment, the pretilt angle is a very vital factor in the alignment process. In general, the surface pretilt angle on the rubbed PI film is merely 1 to 3°. Nowadays, a high pretilt angle is required in order to prevent stripe domains in super twisted nematic LC displays (STN-LCD). Therefore, it is necessary to develop novel alignment materials and methods to meet the requirements of the high performance LCDs' development. According to recent reports, high pretilt angles can be generated by structural modification of the PI backbone with polar moieties(13, 14).

Reorientation effects based on the photo-induced *trans/cis* isomerization of azobenzene (Azo) units may be used for high-density information storage(15). Further applications include photo-induced alignment of liquid crystals by azobenzenes contained in a surface layer(16). Previously, we investigated the photo-driven LC cells using azobenzene-grafted ladderlike polysilsesquioxanes (LPS) films as command layers(17, 18) and also prepared the LC alignment layers with varied pretilt angles based on modified LPS(19). The overall properties of the LPS such as excellent transparency, mechanical properties, film forming ability and high stability enable this material to be a promising candidate for LCD alignment layer and other applications(20, 21).

In this work, a novel two-step method combining rubbing and UV-irradiation based on LPS containing cinnamate and azobenzene side chains was developed to obtain alignment layers with high pretilt angles. Normally a low pretilt angle of 1–3° was first generated by rubbing and then an increased pretilt angle of 11° was obtained through exposing the rubbed alignment layer to UV light moreover. The increased pretilt angle was stabilized by in situ photo-crosslinking of the photo-sensitive cinnamate side-chains.

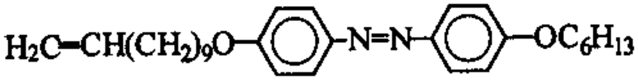
EXPERIMENTAL

Materials

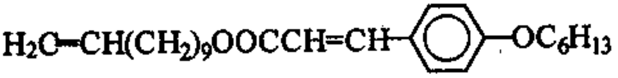
The skeleton polymer material, ladderlike copoly(phenyl-hydrosilsesquioxane) (PPHSQ) with a Phenyl/H mole ratio of 30:70 was synthesized as before(20). The coupling agent, 3-(trimethoxysilyl)propyl methacrylate (KH570) was commercially available. 4-Hexoxy-4′-undec-10-enyloxyazobenzene (6Az11) and 1-undecenyl p-hexoxycinnamate (6Cin11) were synthesized according to the literature(17, 21).

KH-570: $H_2C=C(CH_3)COO(CH_2)_2Si(OCH_3)_3$

6Az11:

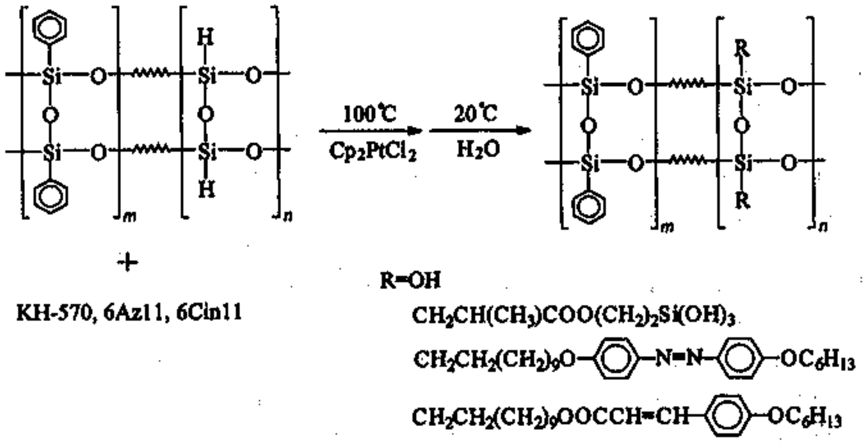


6Cin11:



The P-Az-Cin-KH570 (abbreviation for PPHSQ grafted with 6Az11, 6Cin11 and coupling agent KH570) was synthesized via hydrosilylation as shown in Scheme 1. A Schlenk flask with 24.3 mg (0.054 mmol) 6Az11 and 7.1 mg (0.018 mmol) of 6Cin11 was degassed with dry argon three times. Then 2 mL of toluene solution containing 4.4 mg (0.018 mmol) of KH570 was injected into the flask, into which a 0.2 mL of dichloromethane solution (conc. 1 mg/mL) of dicyclopentadienyl-platinum dichloride (Cp_2PtCl_2) as catalyst, 5 mL of anhydrous toluene and 2 mL of toluene solution (conc. 18 mg/mL; Si-H: 0.18 mmol/mL) of PPHSQ were injected. The solution was stirred at 90°C for 60 hours under the protection of dry argon.

P-Az-KH570 (abbreviation for PPHSQ grafted with 6Az11 and KH570) and P-KH570 (abbreviation for PPHSQ only grafted with KH570) were prepared by hydrosilylation similarly.



SCHEME 1 The structure and synthesis of the modified LPS

Preparation of the alignment layer and cell fabrication

The 4 mg/mL polymer solution was spin-coated on a cleaned quartz plate or ITO glass plate and the film was mildly baked at 80 °C for 15 minutes and then cured at 180 °C for 4 hours. The film was unidirectionally rubbed using a machine equipped with a moving velvet cloth. The loading pressure was 30 g/cm^2 and the velvet was moved unidirectionally at a velocity of 2 mm/s over a distance of 120 cm.

Sandwich-type cells with thickness of 30 ± 1 μm were assembled with two pieces of the surface-modified glass plates keeping the rubbing direction antiparallel to each other. The liquid crystal 4-pentyl-4′-cyanobiphenyl (5CB) (transition temperature of nematic-isotropic $T_{NI} = 35°C$) was filled in by capillary action at 40–50 °C.

The UV-irradiation was carried out by exposing the cell to a 500 W high pressure Hg lamp which provided the UV light intensity of 15 mW/cm^2 at 365 nm on the surface. The pretilt angles of the LCs on the alignment surface were measured by the crystal rotation method(22, 23) at room temperature.

Digital Nanoscope IIIa AFM (atomic force microscope) was used to observe the feature on the surface. The geometry calculation of the *cis*-6Az11 molecule was carried out by Alchem 2000 of version 1.0 from Tripos, Inc. St. Lewis, MO.

RESULTS AND DISCUSSION

Effect of UV-irradiation time

A proper exposure time of 20 minutes was adopted in order to obtain a stable and high pretilt angle. A high pretilt angle can not be obtained during short exposure time perhaps because low exposure energy does not generate crosslinking enough to stabilize the photo-induced *cis*-isomer state. On the other hand, the homogeneous alignment of the LC can be destroyed upon longer exposure time. Figure 1 shows a comparison between the exposed area for different exposure times and the non-exposed area. The good LC alignment can be obtained in the exposed area only for a proper exposure time of 20 minutes (Figure 1a). Meanwhile, the alignment of the LC in exposed area is destroyed and disclination is appeared after a much longer exposure time (Figure 1b).

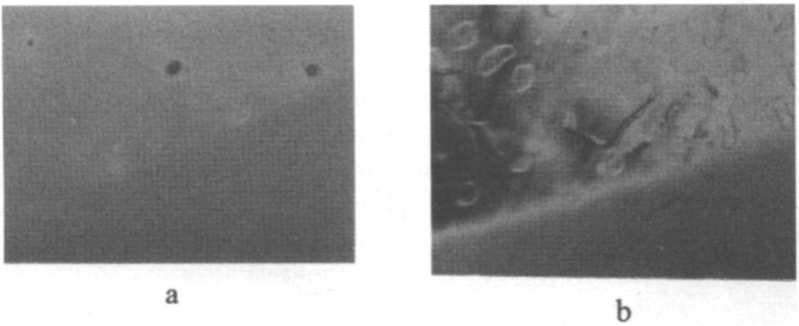


FIGURE 1 The contrast between exposed area and non-exposed area of the alignment layers based on P-Az-Cin-KH570 for different exposure time, a) 20 minutes, b) 60 minutes (See Color Plate III at the back of this issue)

The variation of the pretilt angles by UV-irradiation

Figure 2 shows the variation of the pretilt angles of 5CB on the rubbed LPS film surface before and after UV-irradiation. The original pretilt angles of 5CB are of 1–3° on the rubbed film surface. The pretilt angle on the alignment layer based on P-KH570 without photosensitive side chains is not affected by exposing to non-polarized UV light.

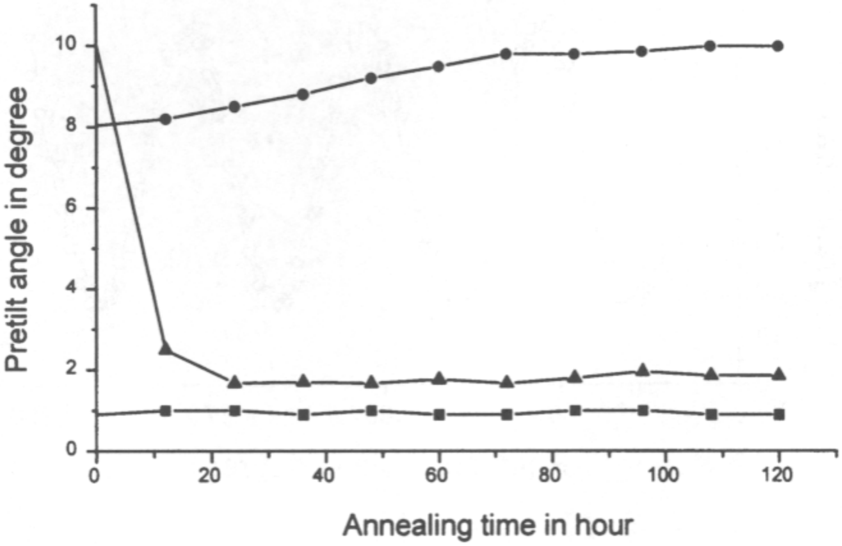


FIGURE 2 The dependence of pretilt angles of 5CB on the alignment layers based on P-Az-KH570 (▲), P-Az-Cin-KH570 (•), and P-KH570 (■) upon annealing time

The pretilt angle of the liquid crystal 5CB on the alignment layer based on photosensitive P-Az-KH570 increased to about 10° after exposure to UV light but the high pretilt angles returned to the original value after one day. co-grafting cinnamate monomer with the azobenzene monomer onto LPS main chains would enhance the stability of the UV-exposure-induced high pretilt angles. It is suggested that the high pretilt angles generated by UV-irradiation are attributed to the *trans/cis* isomerization of the photosensitive groups. Rubbing make side-chains to lie on the LPS film surface at a small slanting angle. After UV-irradiation, the isomerization of the quasi-planar aligned azobenzene side chains make their free-terminal ends erected, and so to make the pretilt angles increase. But it is known that the *cis*-isomer of Azo group is not stable and is easily reversed to its *trans*-isomer, so the high pretilt angles would return to the low original value. When the cinnamate derivatives are co-grafted with azobenzene derivatives onto LPS main chains, the in situ photo-crosslinking of the cinnamate side chains prevents the *cis*-isomer of azobenzene side chains from reversing to its *trans* form, therefore the higher pretilt angle of the nematic LC on the surface is maintained.

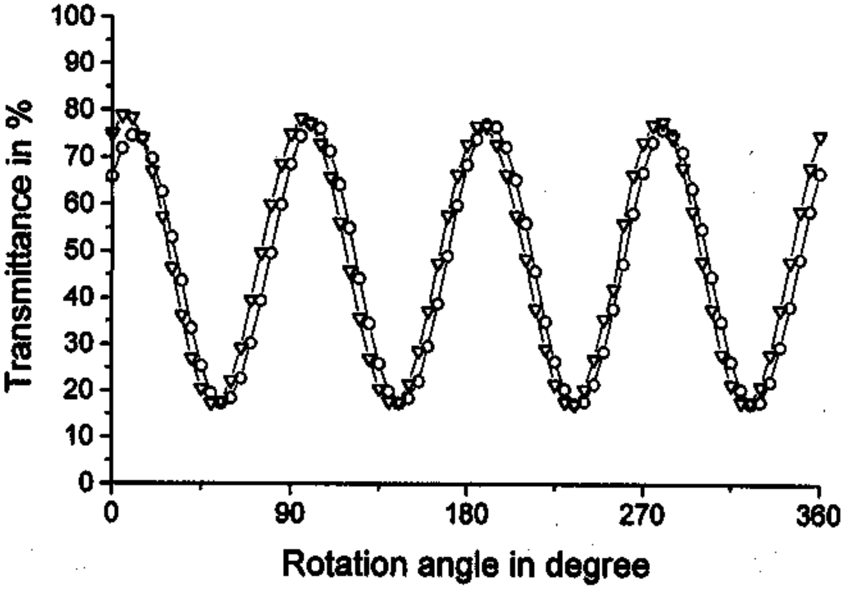


FIGURE 3 Transmittance through crossed polarizers and a homogeneous cell as a function of the rotation angle of the cell about the microscope optical axis in exposed (Δ) and non-exposed (O) areas

Transmittance periodical change observed by polarized microscope

The liquid crystal 5CB filled in an anti-parallel cell was homogeneously oriented. Between crossed polarizers, the cell was bright and dark alternately when the cell was rotated about the optical axis of the microscope. Figure 3 shows the dependence of light transmittance through crossed polarizers upon the rotation angle of the cell. There is no difference before and after exposure. It means that the UV-exposure does not change the homogeneous alignment of the liquid crystal.

Conoscopic pictures

Under conoscopic conditions using a monochromatic sodium lamp, various interference figures for the non-exposed and exposed areas were observed as shown in Figure 4. The off-center families of hyperbolas confirmed that the LCs in the cells are in homogeneous alignment and the director of the LC molecules tilts on the plane of the substrate with different tilt angles.

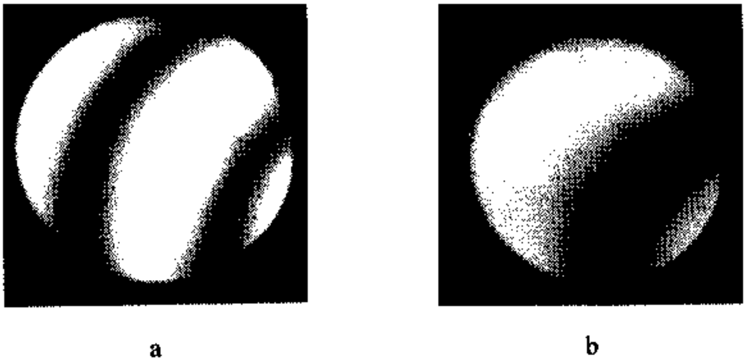
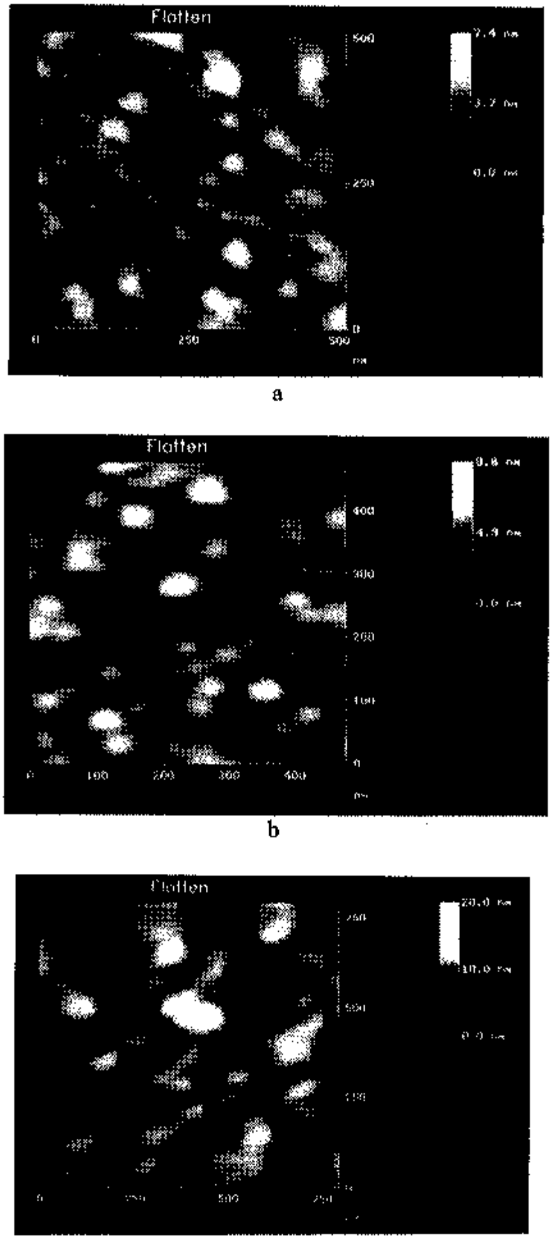


FIGURE 4 Conoscopic pictures of the liquid crystal cells based on P-Az-Cin-KH570, a) non-exposed area, b) exposed area

AFM study

An atomic force microscopy (AFM) study was performed on a P-Az-Cin-KH570 surface before and after UV-irradiation for different time in the contact mode using a Digital Nanoscope IIIa. The top view of the surface topography shown in Figure 5 supports the mentioned above mechanism of the UV-irradiation inducing high pretilt angles. Some convex regions on the surface are observed. After proper UV-irradiation, the number of the bright con-



a

b

c

FIGURE 5 The AFM images of the surface topography of the alignment layers based on P-Az-Cin-KH570 before and after different UV-exposure, a) non-exposed, b) exposed for 20 minutes, c) exposed for 60 minutes vex-regions increases. In addition, the average height of the convex regions also increases from the original 1.2 nm to 2.0 nm after exposure. Figure 6 is the simulation image of a single molecule of *cis*-6Az11. The computer simulation of 6Az11 shows that the length of the vertical fragment of the molecule is about 1.4 nm. It is longer than the average increase in the height of the convex regions. This may be attributed to two reasons: a) the side chain on the film surface is not free as simulated single molecule, its deformation is constrained by other side chains and crosslinking, and b) the terminal alkoxyl fragment is not vertically aligned. The increase in pretilt angle is relative to the increases of the number and the height of the grain-like convex regions observed on AFM image. It is suggested that the convex region is a congregation of the side chains. However, the average diameter of the convex areas increases from 30 nm to more than 100 nm and a homogeneous surface is destroyed after a excess exposure for 60 minutes, which made the LC alignment in disorder and induced the disclination as shown in Figure 1b.

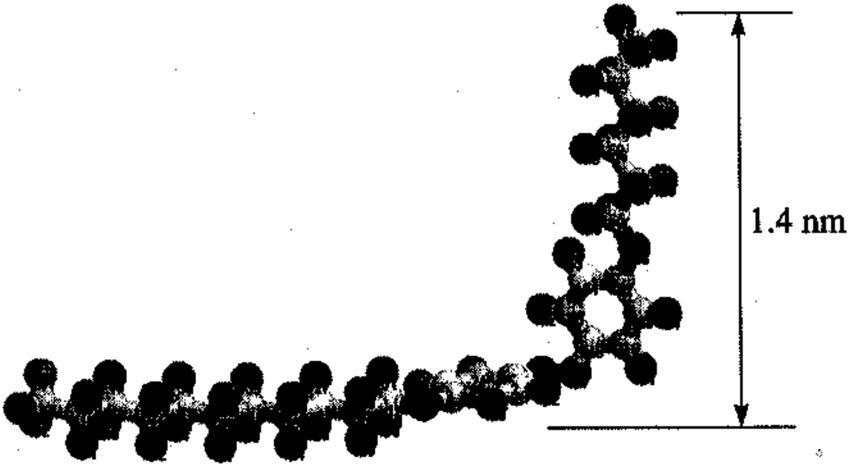


FIGURE 6 The simulation image of the *cis*-6Az11 molecule

In summary, the two-step method combining rubbing and UV-irradiation based on LPS containing cinnamate and azobenzene side chains produces alignment layers with stable and high pretilt angles. The high pretilt state is stabilized by in situ photo-crosslinking of the cinnamate side chains during the UV-irradiation. In particular, the convenient UV-irradiation technique may be used to produce a patterned alignment layer for improving view angle in LCD.

Acknowledgements

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