LIQUID CRYSTALS, 1998, VOL. 25, NO. 6, 757–764

Stable photoalignment layer for nematic liquid crystals based on ladder-like polysilsesquioxanes

LI CUI, WEI JIN, JINNAN LIU†, YONGXIN TANG§, PING XIE
and 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
†Department of Applied Chemistry, Beijing University of Chemical Technology,
Beijing 100029, PR China
§Department of Polymer Science, The University of Akron, Akron, Ohio 44325,
USA

(*Received 23 April 1998; in final form 20 July 1998; accepted 4 August 1998*)

A new kind of aligning material for liquid crystal cells, ladder-like polysilsesquioxanes (LPS) grafted with cinnamoyl side groups, has been developed to improve the thermal stability of the photoalignment layer. The LC aligning ability of the LPS-based alignment layers, fabricated by linearly polarized UV-induced polymerization (LPP), was characterized by polarizing optical microscopy, conoscopic observations and electro-optic response measurements. In particular, a practical and severe annealing test was adopted to examine the thermal stability of the alignment layer; this showed that even when LC cells were annealed at 100°C (much higher than the clearing point of the LC) for several hours, good LC orientation could remain when the cell was cooled to a constant measurement temperature. The results confirmed that the photoalignment layers exhibited not only good LC aligning ability, but also excellent thermal stability, so heralding their potential application in LCDs.

1. Introduction

A key topic for liquid crystal displays (LCDs) is control of the alignment of the LC molecules. Almost in every commercial flat panel LCD, the LC alignment is achieved by confining the LC between two alignment layers made from mechanically rubbed polyimide (PI) films. Nevertheless, the high curing temperature (~300°C) and strongly polar solvent usually employed in the manufacturing process are harmful to the colour filters and the thin film transistors (TFTs) in the LCD devices. Besides, the mechanical rubbing can generate dust and surface charge which can lower the quality of the cells. Therefore, it is necessary to develop novel alignment materials and technologies to meet the requirements of high performance LCD development.

In 1992, Schadt *et al.* [1] first proposed a rubbing-free alignment method based on the linear photopolymerization of polyvinyl cinnamate (PVCN), a procedure which is not only able to overcome some of the drawbacks of rubbing technology, but also improves the viewing angles of LCDs by forming orientation patterns within each display element [2]. Since then, a lot of work [3–16] has been done to modify this photoalignment technique. However, a number of issues have not yet been solved. In particular, the thermal stability of the LC orientation and the adhesion properties of the photoalignment layers are currently problematic. Therefore, it is important to seek good materials to improve the performance of the photoaligment layer.

Schadt *et al.* [17] have improved the thermal stability of photoalignment layers using polymethyl acrylate instead of polyvinyl alcohol as the backbone and obtained photoalignment layers which could withstand 120°C. Yaroshchuk *et al.* [18] obtained photoalignment layers based on single chain polysiloxane cinnamate (PSCN) with improved heat resistance and the quality of the LC orientation remained good up to the clearing

---

*Author for correspondence.

point. There are also reports on PI-based photoalignment layers [7, 19] which, unfortunately, are not good enough to meet application requirements.

To be more practical, we should study LC cells with stable photoalignment layers instead of ITO plates with the photoalignment layers mentioned above. It is obviously necessary to search for a backbone material with excellent comprehensive properties. Fortunately, the ladder-like poly(hydrosilsesquioxane) (H-T) and its copolymers, first synthesized in our laboratory [20], are new types of material with a glass-like skeleton. A new family of functionalized polymers including liquid crystalline [21–23] and non-linear optical (NLO) polymers [24, 25] have been produced via Pt-catalysed hydrosilylation of H-T and its copolymers with alkenes or alkynes. In particular, we have investigated the properties of photodriven LC cells using azobenzene-grafted ladder-like polysilsesquioxane (LPS) as the command layer [26, 27] and prepared the LC alignment layers based on modified LPS through a mechanical rubbing method [28, 29]. They possess not only excellent transparency, mechanical properties and film-forming ability, but also excellent resistance to irradiation and heat. In addition, the LPS can be cured under milder conditions (150–200°C), a process ascribed to condensation between Si–OH groups. Moreover, adhesion can be improved by modifying the LPS with silane coupling agent. Therefore, the materials are suitable for improving the performance of photoalignment layers for liquid crystals.

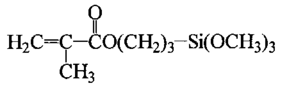
In this paper, we report the synthesis of photosensitive LPS containing cinnamoyl side groups and the alignment behaviour of a LC sandwiched between two such LPS-based photoalignment layers. A practical method, an annealing test, was adopted to investigate the thermal stability of the cells carrying the LPS-based alignment layers.

2. Experimental

2.1. *Materials*

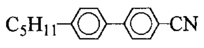
Undec-10-enol was prepared according to our previous report [30]. *p*-Hexyloxybenzaldehyde was prepared by a Williamson reaction of *p*-hydroxybenzaldehyde and 1-bromohexane. Before use, tetrahydrofuran (THF) was heated under reflux over sodium sand and distilled, and pyridine was heated over potassium hydroxide and distilled. All other reagents and chemicals were commercially available and used as purchased without further purification.

The nematic liquid crystals, 5CB ($T_{NI} = 35°C$) and TEB30 (LC temperature range: -10 to 60°C) were purchased from the Liquid Crystal Materials Company of Tsinghua University (Beijing, China). The silane coupling agent, KH570, was commercially available. The structures of the materials and mixture components are shown below:

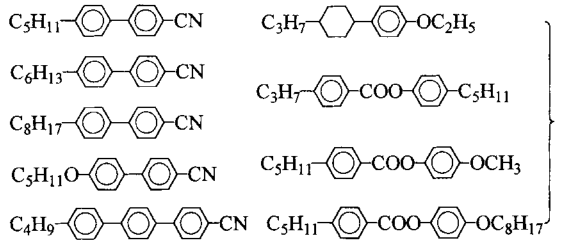


$H_2C{=}C(CH_3){-}\overset{O}{\overset{\|}{C}}O(CH_2)_3{-}Si(OCH_3)_3$

KH570



5CB



TEB30

2.2. *Synthesis*

2.2.1. *Cinnamoyl monomers*

These were synthesised as shown in figure 1. Typically, undec-10-enyl *p*-methoxycinnamate was synthesised in the following way.

2.2.1.1. *Synthesis of p-methoxycinnamic acid* [31]

As described in [31], a few drops of piperidine were added to a solution containing 6.8 g (0.05 mol) of anisaldehyde, 5.2 g (0.05 mol) of malonic acid and 11.85 g (0.15 mol) of pyridine. The solution was heated to 90°C and stirred for 2.5 h, whereon the temperature was raised to 115°C and refluxed until no more bubbles of CO_2 were produced. The solution was cooled to room temperature and poured into 40 ml of an aqueous solution containing 10 ml of concentrated hydrochloric acid; the white solid was collected and dried. The crude product was recrystallized twice from ethanol to give the required product in 65% (5.8 g) yield. The product exhibits a nematic phase in the range 174 to 188°C.

^1H NMR (200 MHz, $CDCl_3$) δ(ppm): 3.8 (s, 3H, CH_3), 6.3 (m, 1H, $Ar{-}C\underline{H}{=}CH$), 6.9 (m, 2H, Ar–H), 7.5 (m, 2H, Ar–H), 7.7 (m, 1H, $Ar{-}CH{=}C\underline{H}$). Elemental analysis. Calc for $C_{10}H_{10}O_3$: C 67.41, H 5.66. Found: C 67.35, H 5.55%.

2.2.1.2. *Synthesis of p-methoxycinnamoyl chloride*

To a flask equipped with a reflux condenser and gas absorber and containing 17.8 g (0.1 mol) of *p*-methoxycinnamic acid, 7.5 ml (12.3 g, 0.105 mol) of thionyl chloride was added dropwise with stirring. The temperature was kept at 70°C for 7 h. The residual thionyl chloride and acidic gases were removed with dry argon, and the crude product was distilled under vacuum to give the product in 90% (17.68 g) yield, b.p. 148–150°C/2 mm Hg.

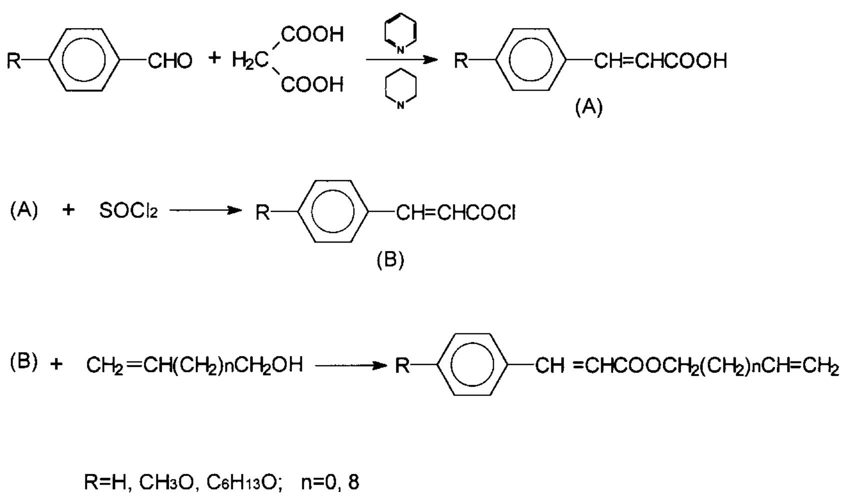


Figure 1. Synthetic route to the cinnamoyl momomers.

2.2.1.3. *Synthesis of undec-10-enyl p-methoxycinnamate*

A THF solution containing 3.92 g (0.02 mol) of *p*-methoxycinnamoyl chloride was added dropwise to 15 ml of a THF solution containing 3.4 g (0.02 mol) of undec-10-enol and 4 ml of pyridine. The solution was heated to 50°C and stirred for 12 h, and then cooled and poured into 70 ml of water. The solution was shaken with diethyl ether (2 × 10 ml) and the combined ether extracts were washed with 50 ml of water and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the resulting liquid distilled under vacuum to produce the required product in 65% yield, b.p. 245–248°C/2 mm Hg.

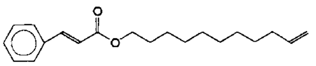
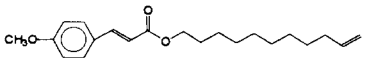
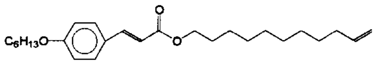
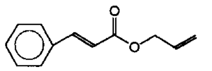
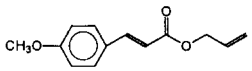
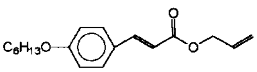
^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 1.2–1.5 (s, 12H, $(C\underline{H}_2)_6CH_2CH=CH_2$), 1.62–1.74 (t, 2H, $COOCH_2C\underline{H}_2$), 1.96–2.1 (t, 2H, $C\underline{H}_2CH=CH_2$), 3.9 (s, 3H, CH_3), 4.2 (t, 2H, $COOCH_2$), 4.9–5.0 (t, 2H, $CH=C\underline{H}_2$), 5.7–5.9 (m, 1H, $C\underline{H}=CH_2$), 6.3 (m, 1H, Ar–$C\underline{H}=CH$), 6.9 (m, 2H, Ar–H), 7.5 (m, 2H, Ar–H), 7.7 (m, 1H, Ar–$CH=C\underline{H}$).

Other cinnamoyl monomers were synthesized similarly; the structures of all the monomers were characterized by IR and ^{1}H NMR. The basic characterization data are shown in table 1.

2.2.2. *Synthesis of the ladder-like polysilsesquioxane*

The ladder-like copoly(methylhydrosilsesquioxane) (PMHSQ) was prepared according to our previous report [20]. The mole ratio of CH_3 : H in PMHSQ is 40 : 60 calculated from the volume of hydrogen discharged when a certain weight of the polymer is reacted with an excess of aqueous sodium hydroxide.

Table 1. Data for the cinnamoyl monomers.

Compound	Structure	b.p./°C/mm Hg	Yield/%
Cin11		218-220/7	77
1Cin11		245-247/2	65
6Cin11		263-265/1	65
Cin3		140-142/8	68
1Cin3		162-164/3	70
6Cin3		200-202/2	64

2.2.3. *Synthesis of the cinnamoyl-grafted PMHSQ*

PMHSQ-Cin-KH 570 (abbreviation for PMHSQ grafted with cinnamoyl monomers and coupling agent KH570) was synthesized by hydrosilylation as shown in figure 2. A Schlenk flask containing 12 mg (0.36 mmol) of 1Cin11 was degassed with dry argon three times before 2 ml of a toluene solution containing 6.8 mg (0.36 mmol) of KH570 was injected into the flask, followed by 0.2 ml of a dichloromethane solution (conc. 1 mg ml^{-1}) of dicyclopentadienyl-platinum dichloride (Cp_2PtCl_2) as catalyst, 5 ml of anhydrous toluene and 2 ml of a toluene solution (conc. 18 mg ml^{-1}; Si–H: 0.18 mmol ml^{-1}) of PMHSQ. The solution was stirred at 90°C for 60 h under a dry argon atmosphere.

PMHSQ-Cin (abbreviation for PMHSQ grafted only with cinnamoyl monomers) materials were prepared similarly by hydrosilylation.

2.3. *Fabrication of the alignment layer*

The quartz plates ($1.5 \times 2.5\,cm^2$) or ITO glass plates ($1.25 \times 2.5\,cm^2$) were cleaned ultrasonically in the following sequence with acetone, 20 wt. % sodium hydroxide solution, saturated aqueous sodium bicarbonate and distilled water, followed by drying at room temperature. Then a 4 mg ml^{-1} toluene solution of PMHSQ-Cin was spin-coated on the quartz or ITO glass plates at 1500 rpm. The thin film was exposed to 365 nm polarized UV light. A Glan–Taylor prism in series with a 500 W high-pressure mercury lamp provided polarized UV light with ~10 mW cm^{-2} of light intensity on the surface of substrate. An 8 µm thick polyethylene film was used as spacer between two such surface-modified quartz or ITO glass plates. The liquid crystal (TEB30 or 5CB) was filled in by capillary action.

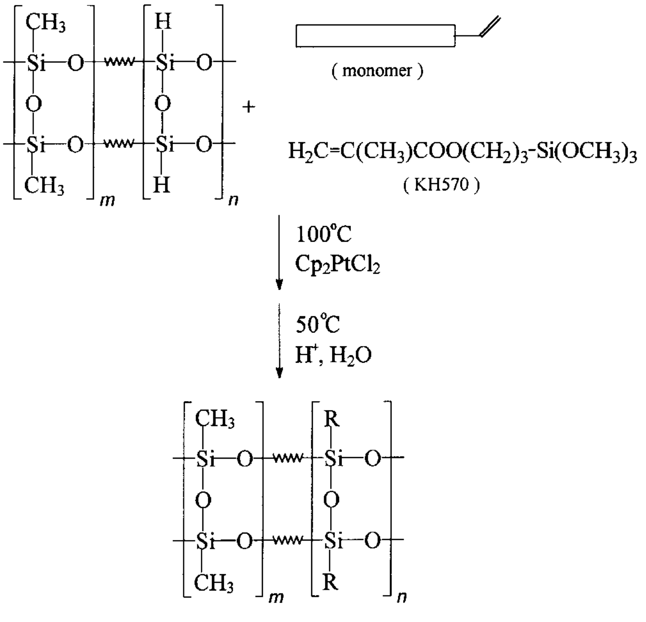


Figure 2. Synthesis of PMHSQ with grafted cinnamoyl side groups.

2.4. *Measurements*

A polarizing optical microscope equipped with an amplifier in series with a photodiode or a camera was used to detect the light intensity and take photographs. The conoscopic pictures were taken using crossed polarizers with an inserted condensing lens and Bertrand lens; a sodium lamp was used as the monochromatic light source. The electro-optic response was determined using a standard measurement system. Antiparallel cells were assembled with the LPP-film-modified ITO glass substrates and filled with TEB30. The potential applied to the cell was controlled by computer and the light intensity transmitted through the cell was detected by the photodiode and recorded by the computer simultaneously.

3. **Results and discussion**

3.1. *Characterization of the alignment state*

A good alignment state of the LC molecules in the cells could be obtained under optimized cell fabrication conditions. Figure 3 shows a comparison between the exposed area and the unexposed area of a LC cell viewed by polarizing optical microscopy (POM). The left part of figure 3(*a*) and the upper part of figure 3(*b*) show unexposed areas. They had general nematic textures and some disclinations. The right part of figure 3 (*a*) and the lower part of figure 3 (*b*) show areas exposed to polarized UV light and have a uniform orientation of the LC molecules. The bright exposed area [in figure 3 (*a*)] became dark [in figure 3 (*b*)] when the LC cell was turned clockwise through 45 degrees, while the unexposed area was unchanged. Comparison of the exposed and unexposed areas indicated that the LC molecules in the exposed area were in homogeneous alignment.

The conoscopic figures obtained from the cells were observed to distinguish the alignment state of the LC molecules in the cell. Figure 4 is the conoscopic figure from the exposed area of the cell in figure 3. An eccentric interference streak was observed. From the direction of the eccentricity it could be deduced that the LC molecules were aligned perpendicular to the direction of the electric field vector **E** of the incident linearly polarized UV radiation. The result demonstrated that the LC molecules in the exposed area were in homogeneous alignment, confirming the former result.

The dependence of the transmittance upon rotation angle of the same LC cell is shown in figure 5. The alternate appearance of peaks and valleys in the transmittance at every 90 degree interval shows that the

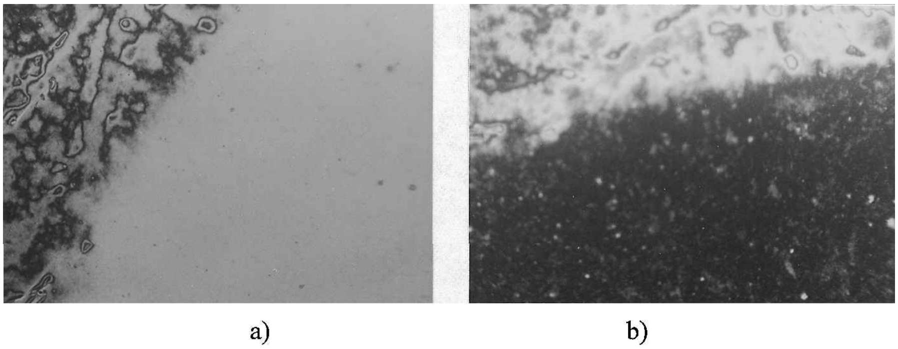


Figure 3. Photomicrographs obtained by POM of the cell assembled with quartz glass plates, modified using PMHSQ-1Cin11; the uniformly bright exposed area (*a*) became dark (*b*) when the LC cell was rotated through 45 degrees.

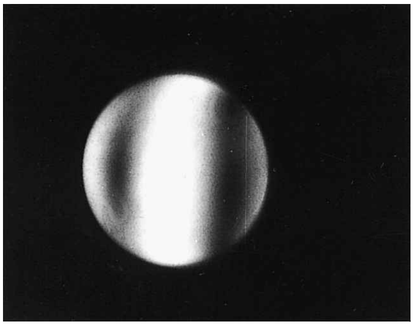


Figure 4. Conoscopic image of the same cell as that in figure 3 showing the LC in the exposed area was in a homogeneous state.

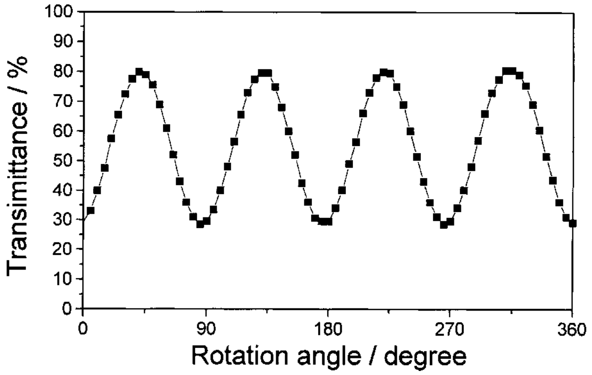


Figure 5. Angular dependence of transmittance for an anti-parallel LC cell assembled with ITO glass plates modified using PMHSQ-1Cin11, after 50 min irradiation with linearly polarized UV light.

transmittance is a function of $\sin^2(2\phi)$. This means that a uniaxial alignment of the LC molecule was induced by the polarized UV irradiation.

According to the literature [6, 13, 31, 32], the anchoring energy of photoalignment layers was found to be $\sim 10^{-6}$ J m^{-2}, which is less than that for alignment layers made by a typical rubbing method ($\sim 10^{-5}$ J m^{-2}). It could be assumed that the better and more stable alignment of LCs on the alignment surface would exhibit a higher anchoring energy. In addition, according to [13], a stronger birefringence of the alignment layer corresponds to a higher anchoring energy. Based on the good alignment state shown in the POM photographs and the azimuthal dependence of the transmittance in figure 5, as well as the good stability of the alignment layer which will be discussed later, it is estimated that the anchoring energy of the LPS-based photoalignment layer was not less than 10^{-6} J m^{-2}.

The electro-optic response of the cell is shown in figure 6. When the potential changed from zero to 10 V applied in the form of a 500 Hz square wave, the homogeneous state converted to the homeotropic state, and the transmittance of the cell decreased. When the applied potential returned to zero, the alignment of the LC molecules recovered to the homogeneous state. The on-time was about 20 ms and the off-time was about 45 ms.

All the above results demonstrate that the LC molecules in the cells fabricated with the LPS-based photoalignment layers were in a planar alignment of good quality.

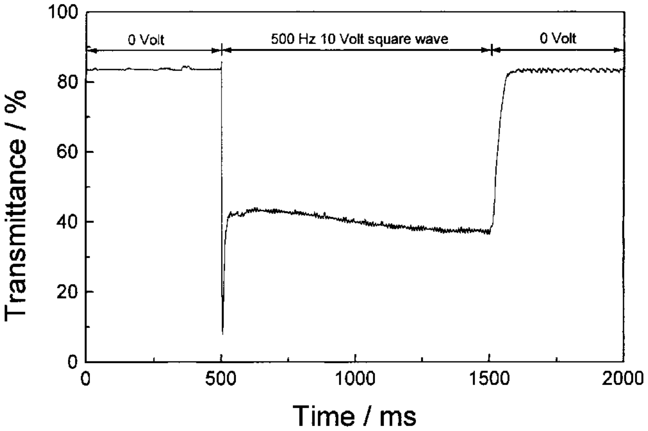


Figure 6. The electro-optical response of the same cell as that in figure 5 to a 500 Hz, 10 V square wave potential.

3.2. *Influence of the side group structures*

3.2.1. *The influence of spacers*

As mentioned above, the alignment state can be characterized by the azimuthal dependence of the transmittance [33, 34]. The LC cell with the photoalignment layers was rotated between crossed polarizer and analyser with the electric vector of the polarized light representing the 0° reference axis. For a given rotation angle ϕ, the intensity of the optical transmission $I(\phi)$ for a perfectly aligned uniaxial system is expected to follow the equation:

$$I(\phi)/I(45°) = \sin^2(2\phi) \qquad (1)$$

In fact, $I(\phi)/I(45°)$ reached the minimum value, i.e. $[I(\phi)/I(45°)]^{-1}$ reached the maximum value, when $\phi = n\pi/2$, where $n = 0, 1, 2, 3, \ldots$. Therefore, the value of $[I(\phi)/I(45°)]^{-1}$ can be taken to represent the ordered orientation of the LC in the cell.

The relation between $[I(0°)/I(45°)]^{-1}$ of a LC cell and the exposure time was measured to study the influence of irradiation energy on the alignment efficiency. The results are shown in table 2.

The preliminary results demonstrate that the appropriate exposure time was about 30 min for the LPS grafted with photosensitive monomers with short spacers such as those in 1Cin3 and 6Cin3, while for the LPS grafted with photosensitive monomers with long spacers such as 1Cin11 and 6Cin11, longer exposure time were required.

We suggest that the photopolymerization initiated by the polarized UV light includes two steps whereby (*a*) the strong dichroism of the absorption of actinic light by the photosensitive groups causes the anisotropic azimuthal distribution of the side groups, (*b*) some of the oriented side groups become crosslinked *in situ* due to photocycloaddition between photosensitive groups (here involving the carbon–carbon double bonds of the cinnamoyl side groups). The side groups with longer spacers have a larger entropy than those with shorter spacers and perhaps become mutually intertwisted. Therefore it is more difficult for the side groups with longer spacers to align in the linear photopolymerization process. This may probably explain why the LPS grafted with photosensitive groups bearing longer spacers need longer exposure times.

Table 2. Influence of exposure time upon $[I(0°)/I(45°)]^{-1}$ of the cells.

	LPP time/min					
Compound	10	20	30	40	50	60
1Cin11	7.8	10.6	14.5	22.5	33.9	—[a]
6Cin11	6.6	8.9	12.6	17.8	24.5	—[a]
1Cin3	11.5	21.5	27.2	—[a]		
6Cin3	13.7	16.7	20.6	—[a]		

[a] Homeotropic state

3.2.2. *The influence of end groups*

The POM observations demonstrated that the cell assembled with photoalignment layers made from the LPS with shorter end groups in the side groups had fewer alignment defects than those with longer end groups. LC molecules on the surface of the photoalignment layer are aligned due to the anisotropic interaction between the LC molecules and the side groups on the alignment surface. The longer end groups may be spread out easily in different directions due to their flexibility, and so the uniaxial alignment of the LC molecules may be more or less destroyed. This would introduce more disclinations in the cells using LPS-based photoalignment layers with longer end groups in the side groups.

3.3. *Alignment stability*

In comparison with the usual carbon–carbon main chain polymers containing cinnamoyl side groups, the double chain ladder-like polysiloxanes used in this study are a new type of glass-like skeleton material with excellent overall properties, especially irradiation resistance and thermal stability. In addition, the LPS can be modified easily by grafting different side groups to meet different requirements. The coupling agent grafted on the ladder-like main chains may enhance the adhesion properties of the alignment layers.

In our previous paper, it was confirmed that the LPS film adhered firmly on the substrate after curing [26–28]. In addition, the LPS film has good resistance to UV irradiation. Both of the above are beneficial to improved performance of the LPS-based photoalignment layer.

Yaroshchuk *et al.* [18] reported the dependence of the birefringence of PSCN-based LPP film on temperature, and demonstrated the high thermal stability of the optical anisotropy of PSCN film in comparison with PVCN-based LPP films. Meanwhile, instead of using only the above mentioned temperature scan method for LPP film, a more practical method used in the LCD industry and a severe test condition was adopted to examine the thermal stability of the LPS-based LPP films in this study. The annealing test comprehensively demonstrated the following facts: (*a*) the thermal stability of the LPP film, (*b*) the anchoring stability of the LC on its surface, (*c*) the chemical and adhesion stability of the LPP film on the ITO substrate immersed in the LC at high annealing temperature.

The cells were annealed at much higher temperatures than the clearing point of the LC and then cooled to constant temperature (20°C) to determine the value of

$[I(0^\circ)/I(45^\circ)]^{-1}$ of the cells after a certain time interval. The annealing curves at 75°C and 100°C are shown in figure 7.

Figure 7 (*a*) shows the curves after annealing at 75°C. The orientation of the LCs in cells having an alignment layer without coupling agent (PMHSQ-1Cin11) increased initially and then tended to a high equilibrium value for a long time of annealing. The orientational order for the cells with an alignment layer bearing the coupling agent (PMHSQ-1Cin11-KH570) was lower at the beginning than for PMHSQ-1Cin11, but kept almost level for long annealing times. Even when the annealing temperature was increased to 100°C, the values decreased slowly and the orienting ability of the alignment layer was retained for several hours. This showed that the alignment layer bearing the coupling agent had better stability, possibly due to its better adhering ability and the higher cross linking of the layer.

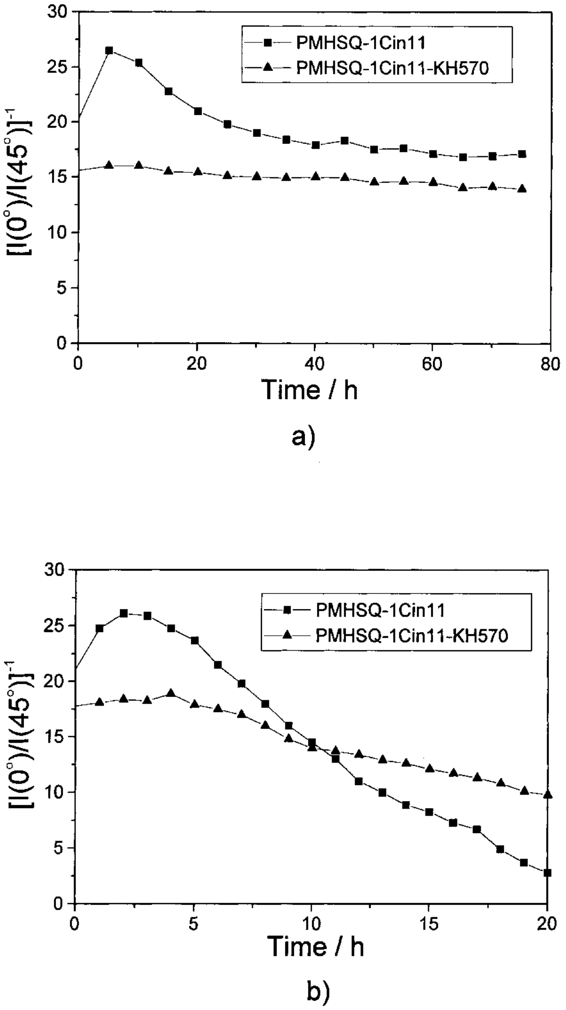


Figure 7. $[I(0^\circ)/I(45^\circ)]^{-1}$ of the cells made using PMHSQ-1Cin11 and PMHSQ-1Cin11-KH570 as a function of annealing time at (*a*) 75°C and (*b*) 100°C.

In comparison with the general method of determining the temperature dependence of the birefringence of the alignment layers [17, 18], the annealing test used in this study was more strict and practical, because the alignment layers must resist not only high temperature deformation, but also etching by the liquid crystal in the cells. The above results have demonstrated the much higher thermal stability of the LC orientation induced by LPS-based photoalignment layers, a result that may be attributed to the excellent adhering ability and heat resistance of the double chain LPS materials. The good thermal stability of the LPS-based photoalignment layers and their ability to control the orientation of the LCs may give them potential for application in LCDs.

4. Conclusion

Double chain LPS-based photoalignment layers provide homogeneous alignment of good quality. A prominent advantage of this type of alignment material lies in its high thermal stability and good adhesion properties to the substrates. Now, we are further improving the performance of the photoalignment layer and endeavour to obtain a satisfactory pretilt angle through introducing other photosensitive groups such as azobenzene moieties by copolymerization.

This project was supported by NSFC (No. 29574187 and 2967400).

References

[1] Schadt, M., Schmitt, K., Kozinkov, V., and Chigrinov, V., 1992, *Jpn. J. appl. Phys.*, **31**, 2155.
[2] Schadt, M., Seiberle, H., and Schuster, A., 1996, *Nature*, **381**, 212.
[3] Kawatsuki, N., Ono, H., Takatsuka, H., Yamamoto, T., and Sangen, O., 1997, *Macromolecules*, **30**, 6680.
[4] Rajesh, K., Masuda, S., Yamaguchi, R., and Sato, S., 1997, *Jpn. J. appl. Phys.*, **36**, 4404.
[5] Tomita, H., Kudo, K., and Ichimura, K., 1996, *Liq. Cryst.*, **20**, 171.
[6] Vorflusev, V. P., Kitzerow, H. S., and Chigrinov, V. G., 1995, *Jpn. J. appl. Phys.*, **34**, L1137.
[7] Rich, D. C., Sichel, E. K., and Cebe, P., 1996, *Polym. Prepr.*, **37**, 809.
[8] Schadt, M., Seiberle, H., Schuster, A., and Kelly, S. M., 1995, *Jpn. J. appl. Phys.*, **34**, L764.
[9] Ichimura, K., Akiyama, Y., Kudo, K., and Hayashi, Y., 1997, *Macromolecules*, **30**, 903.
[10] Dyaduysha, A., Khizhnyak, A., Marush, T., and Reshetnyak, V., 1995, *Jpn. J. appl. Phys.*, **34**, L1000.
[11] Dyadyusha, A., and Reznikov, Y., 1995, *Mol. Cryst. Liq. Cryst. Sci. Technol. C*, **5**, 183.
[12] Chen, J., Johnson, D. L., Bos, P. J., and Sprunt, S., 1996, *Appl. Phys. Lett.*, **68**, 885.
[13] Bryan-Brown, G. P., and Sage, I. C., 1996, *Liq. Cryst.*, **20**, 825.
[14] Hashimoto, T. *et al.*, 1996, 22nd Japanese LC Conference (Kyushu) 2A17; Saitoh, T. *et al.*, 1996, 22nd Japanese

LC Conference (Kyushu) 1A09; Endo, H. *et al*., 1996, IDW'96 (Kobe) 1, 341.

[15] Sun, H., Zheng, C. Y., Tang, H., and Gao, H. J., 1997, *Adv. Disp*., **2,** 18.

[16] Yoshida, H., and Koike, Y., 1997, *Jpn. J. appl. Phys*., **36,** L428.

[17] Schadt, M., Seiberle, H., Schuster, A., and Kelly, S. M., 1995, *Jpn. J. appl. Phys*., **34,** 3240.

[18] Yaroshchuk, O., Pelzl, G., Pirwitz, G., Reznikov, Y., Zaschke, H., Kim, J. H., and Kwon, S. B., 1997, *Jpn. J. appl. Phys*., **36,** 5693.

[19] Rich, D. C., Sichel, E., and Cebe, P., 1997, *J. appl. Polym. Sci*., **65,** 1151.

[20] Xie, Z. S., Jin, S. Z., Wan, Y. Z., and Zhang, R. B., 1992, *J. Polym. Sci*., **10,** 361.

[21] Xie, P., Wan, Y. Z., Zhou, B. S., Hou, J. A., Dai, D. R., Li, Z., Liu, D. S., and Zhang, R. B., 1996, *Macromol. Chem. Phys*., **197,** 745.

[22] Zhang, R. B., Xie, Z. S., Wan, Y. Z., Jin, S. Z., and Hou, J. A., 1993, *Chin. J. Polym. Sci*., **11,** 210.

[23] Wan, Y. Z., Huan, Y. X., Xie, P., Li, B., Jin, S. Z., Cao, X. Y., Liu, D. S., Dai, D. R., Li, Z., and Zhang, R. B., 1996, *Macromol. Symp*., **105,** 249.

[24] Xie, P., Guo, J. S., Dai, D. R., Jin, S. Z., Liu, D. S., Li, Z., and Zhang, R. B., 1996, *Mol. Cryst. liq. Cryst*., **289,** 45.

[25] Xie, P., Guo, J. S., Dai, D. R., Jin, S. Z., Liu, D. S., and Li, Z., 1996, *Polym. adv. Technol*., **7,** 98.

[26] Tang, Y. X., Liu, D. S., Xie, P., and Zhang, R. B., 1996, *Macromol. Rapid Commun*., **17,** 759.

[27] Tang, Y. X., Xie, P., Liu, D. S., and Zhang, R. B., 1997, *Macromol. Chem. Phys*., **198,** 1855.

[28] Tang, Y. X., Cui, L., Xie, P., and Zhang, R. B., 1997, *Macromol. Chem. Phys*., **198,** 3377.

[29] Xie, P., Cui, L., Tang, Y. X., and Zhang, R. B., 1997, *Chinese Patent, Application No. 97112539.2*.

[30] Zhang, S. Y., Bi, S. W., Xie, P., and Zhang, R. B., 1991, *Chin. J. Polym. Sci*., **9,** 195.

[31] Yamaguchi, R., and Sato, S., 1996, *Jpn. J. appl. Phys*., **35,** L937.

[32] Li, X. D., Pei, D. H., Kobayashi, S., and Iimura, Y., 1997, *Jpn. J. appl. Phys*., **36,** L432.

[33] Herz, W., 1945, *J. Am. chem. Soc*., **67,** 1854.

[34] Born, M., and Wolf, E., 1975, *Principles of Optics*, 5th Edn. (New York: Pergamon Press), p. 694.