

Photosensitive Materials on a Base of Polysiloxane for the Alignment of Nematic Liquid Crystals

Oleg YAROSHCHUK, Gerhard PELZL¹, Grit PIRWITZ¹, Yuriy REZNIKOV, Horst ZASCHKE¹, Jong-Hyun KIM² and Soon Bum KWON²

Institute of Physics, National Academy of Sciences, prospect Nauky, 46, Kyiv, 252022 Ukraine

¹*Institute of Physical Chemistry, Martin-Luther-University, Muehlpforte, 1, 06108 Halle, Germany*

²*LCD Lab. of LG Electronics, 533 Hogae-dong, Dongan-gu, Anyang-shi, Kyongki-do 430-080, Korea*

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The light-induced alignment of a number of commercial liquid crystals (LC) on the surface of photosensitive polysiloxane based polymers was studied. It was shown that the materials can provide thermostable homeotropic, planar and tilted alignments of good quality. The value of tilt angle depends upon the LC material, irradiation intensity and exposure as well as aligning film thickness and temperature treatment.

KEYWORDS: liquid crystal displays, liquid crystal alignment, photosensitive polymers

1. Introduction

Homogeneous aligning of liquid crystals (LC) is one of the necessary conditions for the normal operation of LC displays. The traditional technique of rubbing on isotropic polymeric alignment layers does not satisfy increasing demands for alignment quality. Therefore the development of new techniques that do not involve rubbing for LC alignment and aligning materials has generated considerable interest in the last few years.^{1–3)}

One of the new promising alignment techniques is based on the use of photopolymer films.^{4–10)} The aligning ability of these materials is determined by an anisotropies induced by light illumination. Photopolymers are believed to allow the development of “clean”, contactless methods of LC alignment. They control the direction of an easy axis orientation on the aligning surface as well as the azimuthal anchoring energy value.

Some classes of photoaligning materials have recently been developed and studied.^{4–10)} Nevertheless a number of important problems have not yet been solved. In particular, the thermostability of LC orientation, adhesive properties of aligning layers, the ability to align obliquely and alignment of some specific LC's are still problematic. Therefore, the search for new photoaligning materials and their investigation are both of current concern.

The aim of this article is to discuss the aligning properties of photosensitive polysiloxanes. The ability of polysiloxanes to provide good homogeneous, oblique or homeotropic orientation of nematic LC is well known.¹¹⁾ In addition the well-known property of siloxanes to bond chemically with a glass surface may enhance the mechanical characteristics of orienting layers. Incorporating the property of light-induced anisotropy in these materials is expected to combine the good aligning ability of polysiloxane matrixes with the advantages of photoaligning materials.

2. Results and Discussion

2.1 Material

We used esters of cinnamic acid as photosensitive pendant group on polysiloxanes. The chemical structure of the basic synthesised material, polysiloxane cinnamate

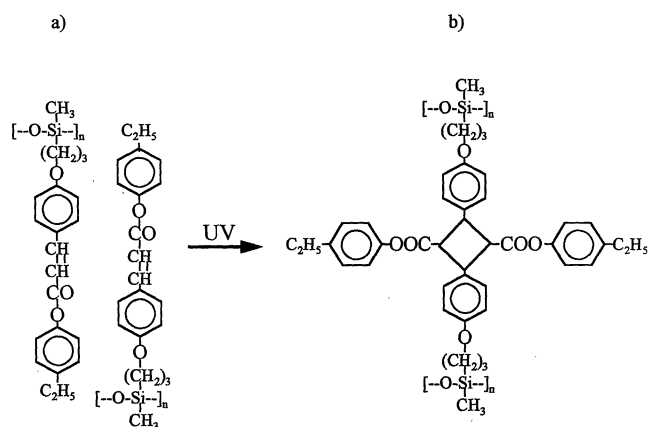


Fig. 1. A polysiloxanecinnamate polymer (a) and its photoproduct (b).

(PSCN), is presented in Fig. 1(a). The method of synthesis of similar materials is described in ref. 12.

PSCN is similar to well known polyvinyl cinnamate polymers¹³⁾ where the polyvinyl-alcohol main chain is substituted for the polysiloxane. As a result, photo-induced chemical reactions in PSCN should be similar to those in polyvinyl cinnamates (PVCN). Namely, the irradiation of PSCN with UV light initiates the cross-linking reaction between cinnamoyl fragments resulting in the production of photo-products depicted in Fig. 1(b).

Strong dichroism of actinic light absorption by photosensitive fragments causes the anisotropic angular distribution of both initial side chains and photo-product fragments after the action of polarised UV light. This leads to a light-induced anisotropy of the irradiated films and the appearance of the axes of easy orientation of LC.^{5,6)}

2.2 Light-induced anisotropy of PSCN

A strong correlation between the aligning properties of the photopolymer and its light-induced anisotropy was found in our early work⁵⁾ as well as in the work of others.^{6,14)} Therefore, we studied the light-induced anisotropy in smectic PSCN films and isotropic PSCN films. Polymer layers 0.1 μm thick were applied by spin-coating a concentrated polymer solution on a glass sub-

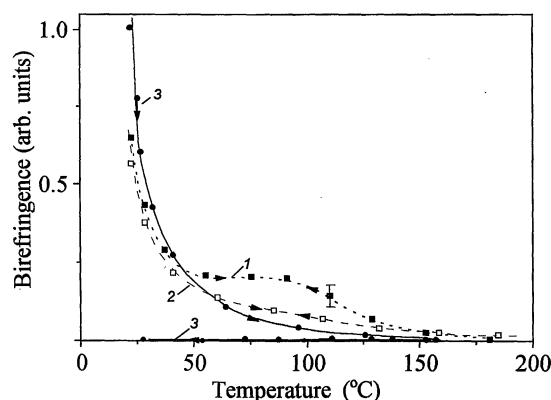


Fig. 2. Behaviour of light-induced birefringence in the photopolymers as a function of temperature: 1: unannealed PSCN layer; 2: annealed ($T_{\text{an}} = 200^\circ\text{C}$, $t_{\text{an}} = 3$ h) PSCN layer; 3: unannealed PVCN layer.

strate at a rotational speed of about 1000 rpm. Smectic PSCN layers were annealed at $T_{\text{an1}} = 50^\circ\text{C}$ for 3 h. Isotropic PSCN layers were produced by annealing at $T_{\text{an2}} = 200^\circ\text{C}$ for 3 h. Light-induced anisotropy was generated in the polymer layers by polarised light irradiation from a mercury lamp (integrated light intensity, $I_{\text{exp}} \approx 6 \text{ mW/cm}^2$).

The dependence of the light-induced birefringence on the temperature is shown in Fig. 2. One can see that changes in birefringence with temperature are reversible up to $T = 200^\circ\text{C}$ for both types of PSCN films. While the dependence $n_a(T)$ is monotonic for isotropic PSCN films, there is an obvious plateau in the curve for smectic PSCN films which coincides in temperature with the interval of the mesophase existence.

The initial optical anisotropy of the smectic phase could not be observed in experiments with smectic PSCN films because the film was thin. Consequently, the observed light-induced anisotropy seems to be provided by the polarisation sensitive photochemical reaction. At the same time, the presence of the orientational ordering in the smectic phase affects the light-induced anisotropy resulting in a different temperature dependence of the light-induced anisotropy.

The results obtained have demonstrated the high thermostability of the induced optical anisotropy of PSCN in comparison with PVCN photopolymer. Our studies of thermostability of the light-induced optical anisotropy of polyvinyl-based photoalignment materials show that it disappears irreversibly when the film is heated up to $T \approx 150^\circ\text{C}$ (see Fig. 2).

2.3 Aligning properties of PSCN

Aligning layers were applied to glass substrates by spin coating of the polymer (rotation speed is 4000 rpm, polymer concentration 2–20 g/l). The thickness, d , of films varied between 50–1000 Å. Substrates were then annealed with either smectic or isotropic PSCN films and subsequently illuminated with polarized light from a Hg-lamp.

Substrates were stuck together by epoxy adhesive (cell thickness $L = 50 \mu\text{m}$ was determined by teflon strips). Cells filled at room temperature were heated to a tem-

Table I. Orientations of different LC's on PSCN substrates.

Liquid crystal	PSCN	
	nonannealed	annealed
MBBA (ISC, Ukraine)	homeotropic	homeotropic
5 CB (ISC, Ukraine)	homeotropic	homeotropic
ZhKM-1282 (NIOPIK, Russia)	homeotropic	homeotropic
ZhKM 440 (NIOPIK, Russia)	planar	planar
ZLI 4801 (MERK, Korea)	homeotropic	tilt/planar

perature close to the LC clearing point, which essentially improved the quality of the orientation.

Orientations obtained for different LC materials on the polymer film investigated are shown in Table I. Various cyanobiphenyls and their compositions as well as MBBA (N-(p-methoxybenzylidene)-p-butylaniline) oriented homeotropically similarly to typical siloxanes.¹¹⁾ The mixture of azobenzene derivatives, ZhK-440, orients planarly. Alignment of all the above mentioned LC compounds is independent of the annealing temperature and radiation exposure. As for the PSCN film—LC ZLI-4801 couple it manifested alternating behaviour: homeotropic alignment was obtained on the smectic PSCN film and planar alignment was found on the initially isotropic PSCN layer. This encouraged us to pursue basic investigation of this pair.

We investigated the dependence of orientation of LC ZLI-4801 on the annealing procedure. For this experiment, films of 50 Å and 800 Å thick were chosen. A number of cells were assembled with substrates differing in annealing time at a given temperature T_{an} . The exposure time, $t_{\text{exp}} = 15$ min, was the same for all samples. Perfect planar or homeotropic alignment appeared to be one of the ultimate orientations. We also observed a variety of transitional cases of alignment differing in tilt angle at different times during annealing.

The tilt angle, θ_{tilt} , was measured by the crystal rotation technique.¹⁵⁾ Dependence of the tilt angle on the annealing time, t_{an} , for two different temperatures, T_{an} , is shown in Fig. 3. The region where the tilt angle drops is very steep. The greater the temperature, the shorter the time was required for the tilt angle to decrease. We did not find a substantial change in the dependence of tilt angle on annealing time for different thickness of film.

The threshold-like behaviour of $\theta_{\text{tilt}}(t_{\text{an}})$ is in good agreement with the data obtained¹⁶⁾ for the rubbed polyimide films. The transition in LC orientation was associated in this work with the decreasing concentration during annealing of the hydrophobic fragments on the surface of the polymer.

We found a strong dependence of tilt angle on the UV light intensity and exposure time. Two sets of substrates with film 50 Å and 1000 Å thick were annealed for 2 h at 200°C . The dependence of $\theta_{\text{tilt}}(t_{\text{exp}})$ for two values of I_{exp} for a film 50 Å thick is shown in Fig. 4. The tilt angle decreases with increasing exposure time. This effect is more rapid at higher intensities. The results observed may indicate that the tilt angle θ_{tilt} is determined by the initial surface density of pendant groups; the decrease in the concentration of these groups with exposure leads to

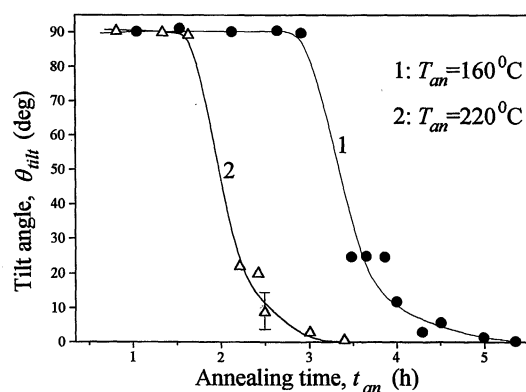


Fig. 3. Dependence of the tilt angle for LC ZLI 4801 on the PSCN surface on annealing time, t_{an} , for two different annealing temperatures: 1: $T_{an} = 160^\circ\text{C}$, 2: $T_{an} = 220^\circ\text{C}$.

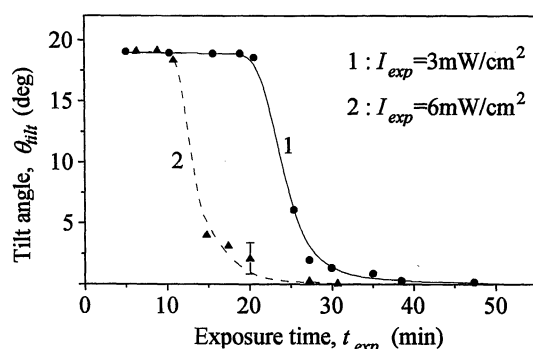


Fig. 4. Dependence of the tilt angle for LC ZLI 4801 on the PSCN surface on exposure time, t_{exp} , for two different intensities of UV light, I_{exp} : 1: $I_{exp} = 3 \text{ mW/cm}^2$, 2: $I_{exp} = 6 \text{ mW/cm}^2$.

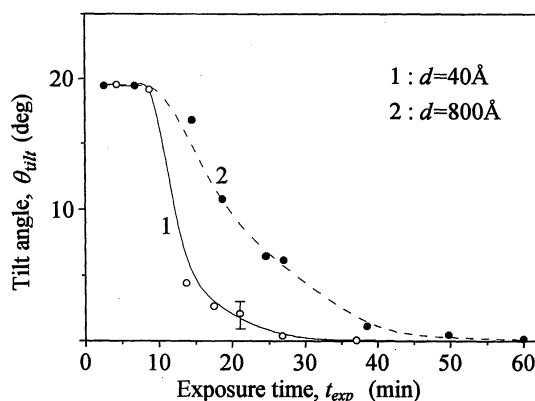


Fig. 5. Dependence of the tilt angle for LC ZLI 4801 on the PSCN surface on exposure time, t_{exp} , for two different layer thickness: 1: $d = 40 \text{ Å}$, 2: $d = 800 \text{ Å}$.

the decreased tilt angle.

Moreover we observed the strong influence of the values of tilt angle on the thickness of the aligning layer. The thicker the layer, the more gradual the decrease of the tilt angle (see Fig. 5), thus we can control the tilt angle smoothly for the latter. This may be the first times a size effect has been observed in a photo-aligning process.

We measured the pretilt angle using combined cells:

one substrate was a PI rubbed alignment layer, the other was photo-aligned layer. From the averaged tilt angle, we could obtain the surface tilt angle of the photo-aligned layer.¹⁰⁾

One of the distinguish feature of the material studied is the high thermostability of photoalignment. The quality of LC orientation remained good up to the clearing point. Few defects appeared while the cell cooled from the isotropic state. The high thermal stability of the tilt was observed for LC compound ZLI-4801; the tilt angle remained constant after the cell was maintained for ten-hours at a the temperature of 85°C ($T_c = 94^\circ\text{C}$).

3. Conclusions

Polysiloxane based photoaligning materials provide homeotropic, planar and tilted alignment of good quality. The value of the tilt angle depends upon the LC, irradiation intensity and exposure as well as the thickness of aligning film and temperature treatment. The high thermostability of the studied materials as well as the ability to control the value of the tilt angle may allow for their wide application in the future.

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