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A novel orientation material for liquid crystals based on modified ladder-like polysiloxanes[a)]

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SUMMARY:

A new orientation material for liquid crystals (LCs) based on modified ladder-like polysiloxanes (LPSs) is investigated. The curing temperature (150–200 °C) of these grafted LPSs is much lower than that of the traditionally used polyimides (PIs) (250–300 °C). The pre-tilt angles of a nematic liquid crystal (LC), 4-pentyl-4′-cyanobiphenyl (5CB), are between 2–8°, depending on the rubbing conditions and the side chains. Annealing experiments at 100 °C and 180 °C demonstrated that the stability of these orientation films is quite well.

Introduction

The pre-orientation status of liquid crystals (LCs) plays a very important role in the performance of liquid crystal displays (LCDs), and this status is strongly dependent on the nature of the substrate surface[1)]. Particularly, the pre-tilt angle between the LC director and the substrate plane significantly influences the optical properties and the dynamic behavior of LCDs[2–5)]. Generally, a pre-tilt angle between 1–4° is required to overcome the reverse tilt which deteriorates the displayed images obviously. In some cases of super-twisted nematic (STN) mode, a higher pre-tilt of ca. 5–8° is preferable to avoid the two-dimensional stripe instabilities[6)] and is essential to realize stable, highly twisted configurations exhibiting very steep transmission-voltage characteristics[7)].

Various materials and methods were studied to obtain such a homogeneous LC alignment with a proper pre-tilt, such as the early oblique evaporation of SiO films[1,8)], the rubbing treatment of polymer films of poly(vinyl alcohol)[1)], polyacrylates[6)], poly(vinyl formal)[9)] and poly(ethylene terephthalate)[10)], polyimide Langmuir-Blodgett films[11)] and the recently developed rub-free, polarized UV/laser irradiation techniques[7,12,13)]. However, polyimides (PIs)[14–20)], which have been studied in detail, are still the materials applied commonly in the LCD industry as orientation media at present, because the processing technology is sufficiently applicable for the manufacture of LCDs, and PIs possess such advantages as chemical and thermal stability, good rigidity, insulation resistance and so on.

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Obviously, PIs have made a great contribution to the LCD industry, however it is not easy for them to produce a high pre-tilt and they require a high curing temperature[6,14], generally between 250–300°C, which is harmful to thin film transistors (TFTs), indium-tin-oxide (ITO) layers and color filters, and hence limits their further applications. Therefore, investigating and developing new orientation materials with a lower curing temperature becomes meaningful.

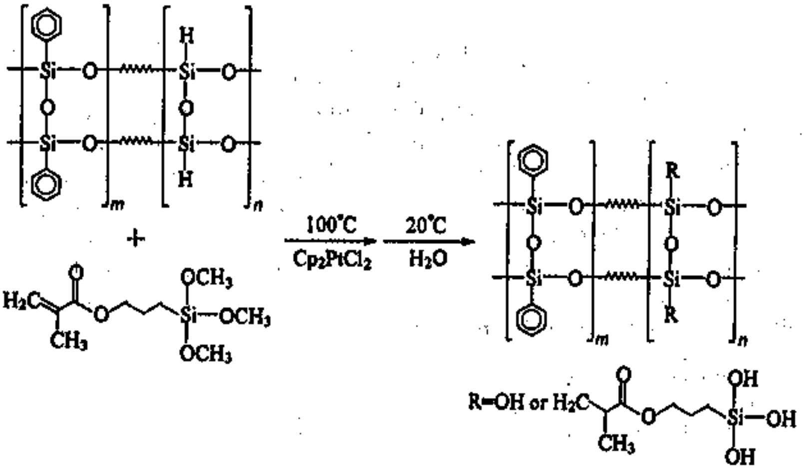
Ladder-like poly(hydrosilsesquioxane) and its copolymers, which were first synthesized in our laboratory[21], are a new type of glass-like skeleton materials. Via hydrosilylation reaction, a variety of functionalized polymers such as liquid crystalline[22-24] and non-linear optical (NLO)[25,26] polymers were developed. Recently, we have successfully used these kinds of polymers grafted with azobenzene (Az) side chains to prepare a command surface for photo-driven LC cells[27,28]. They not only possess excellent transparency, mechanical properties, film-forming ability and resistance to irradiation and heat but also can be cured under milder conditions (150–200°C), ascribed to the condensation between Si—OH groups. A very good orientation state can be obtained without complex treatment, and this state is quite stable to heat. All of these advantages enable this material to be a promising candidate as the orientation medium for LCDs.

Experimental part

Synthesis

The skeleton material, a ladder-like copoly(phenylhydrosilsesquioxane) (PPHSQ) with a phenyl/H mole ratio of 30:70, was synthesized as before[21]. 3-(Trimethoxysilyl)propyl methacrylate (KH-570), a commercially available coupling reagent, was grafted onto the PPHSQ by hydrosilylation reaction, as shown schematically in *Scheme 1*.

Scheme 1:



A Schlenk flask was degassed with dry argon for three times. Then, 1 mL toluene solution (concentration 45 mg/mL; Si—H: 0,538 mmol/mL) of PPHSQ, 9 mL anhydrous toluene, 40 mg of KH-570, 0,2 mL dichloromethane solution (concentration: 1 mg/mL) of dicyclopentadienylplatinum dichloride (Cp_2PtCl_2) as catalyst were injected. The system was stirred at 100°C for 30 h under the protection of dry argon. Then, it was cooled to 20°C and 0,05 mL water was added. The P-570, a PPHSQ grafted with KH-570, was prepared when the system was stirred at 20°C for further 3 h.

The previously studied P3 and P11[28], a ladder-like copoly(methylhydrosilsesquioxane) (PMHSQ) grafted with 4-hexyloxy-4′-prop-2-enyloxyazobenzene (6Az3) or 4-hexyloxy-4′-undec-10-enyloxyazobenzene (6Az11) and vinyltriethoxysilane, were also used here to investigate the influence of side chains upon the pre-tilt angles.

Film preparation, rubbing and cell assembly

A 0,8 wt.-% toluene solution of P-570 (or P3, P11) was spin-coated on cleaned glass plates at 1 500 r.p.m. to form a thin polymer film. Then, the film was cured at 180°C for 8 h.

The rubbing treatment was carried out by pressing the polymer-coated plates down onto a moving rayon cloth in the same way as in ref.[4]. The loading pressure was 40 g/cm^2, and the rayon cloth was moved unidirectionally at a velocity of 2 mm/s over a distance of 3 – 12 m.

A cell was assembled using a 30-μm-thick polyethylene film as spacer between two plates whose rubbing directions were anti-parallel. The liquid crystalline 4-pentyl-4′-cyanobiphenyl (5CB) (transition temperature nematic-isotropic T_{NI} = 35°C) was filled in by capillary action at 40 – 50°C.

Measurement of the pre-tilt angle α_0

The LCs in the anti-parallel cell form a section of a uniaxial single crystal with its optical axis at a small angle α_0, i.e., the pre-tilt angle, with the plane of the plates, and this angle can be measured using the crystal rotation method[2–5]. The cell is placed between crossed polarizers and rotated about an axis which is perpendicular to the optical axis of the LC layer. The incident polarized light makes a 45° angle with the rotation axis. The symmetry point on the curve of transmission versus rotation angle corresponds to the central point of the interference figure, and the pre-tilt angle can be calculated[5].

Results and discussion

Determination of the curing conditions

The cured polymer films have good resistance to erosion with common solvents such as cyclohexanone, acetone and toluene due to the crosslinking among Si—OH groups. Based on the hydrophobicity of the polymer films and the hydrophilicity of the glass surface, the contact angles (θ_c) of drops of water on them were measured before and after the etching, to evaluate the crosslinking extent of the films[18]. Sodium hydroxide aqueous solution was used as the etching agent, since the Si—O bond cleaves under the action of strong bases.

The initial θ_c of all the P-570 films which were cured at 150, 180 or 200°C for different time was about 85°. After etching with a 3 wt.-% sodium hydroxide aqueous solution for 20 min at 16°C and washing with ion-free water, the θ_c decreased to

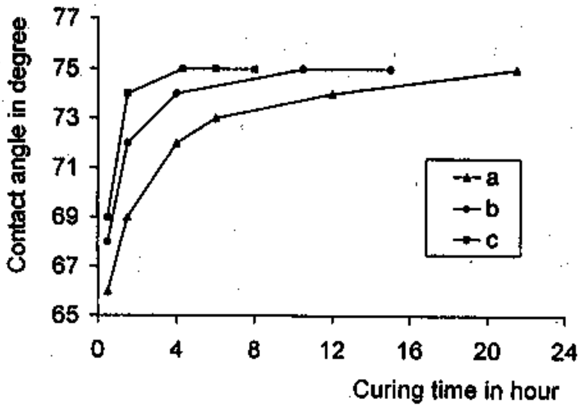


Fig. 1. Contact angle of drops of water on the etched P-570 fims as a function of the curing time at (a) 150°C, (b) 180°C, and (c) 200°C

a certain degree. Fig. 1 shows the relationship between these values versus different curing conditions. The soft and level parts of the curves in Fig. 1 indicate that the θ_c tends to keep unchanged with increasing of the curing time, i.e., the crosslinking is complete. The results also show that this type of polymer can be cured sufficiently at 180–200°C, or even at 150°C.

Orientation status observed by polarizing microscope

The anti-parallel LC cell filled with 4-pentyl-4′-cyanobiphenyl (5CB) was homogeneously oriented. Under crossed polarizers, the cell was bright and dark alternately when the cell was rotated about an axis which was normal to the cell surface and parallel to the optical axis of the microscope. The transmittance ($T_{\%} = I/I_0$, where I_0 is the light transmission through parallel polarizers and an empty cell without LC filled, while I is that through crossed polarizers and a homogeneous LC cell) was recorded using a photodiode detector. Fig. 2 shows the relationship between the light transmittance through crossed polarizers and the rotation angle of the cell. The

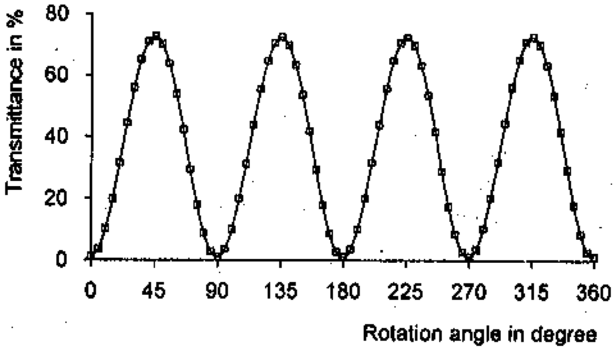


Fig. 2. Transmittance through crossed polarizers and a homogeneous cell as a function of the rotation angle of the cell about the microscope optical axis

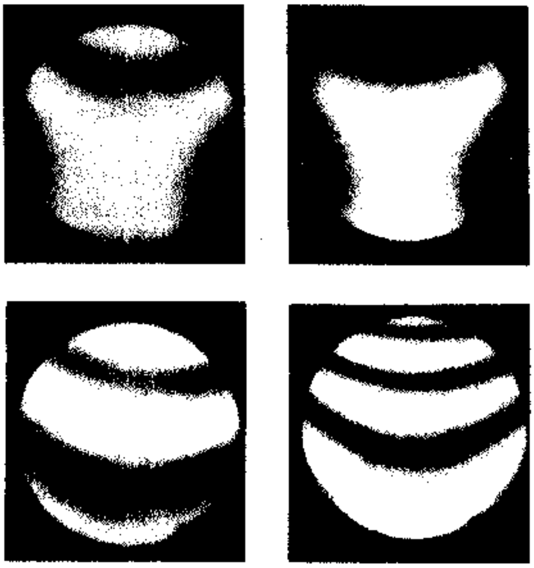


Fig. 3. Various interference figures characterized by families of hyperbolas under conoscopic condition using a monochromatic sodium lamp

maximum and minimum $T_{\%}$ appear when the LC director makes 45° and 0° angles with one of the crossed polarizers, respectively.

Under conoscopic conditions using a monochromatic sodium lamp, various interference figures of some cells were observed, as shown in Fig. 3. The off-center families of hyperbolas confirm that the cell is a homogeneous one and the director of the LC molecules makes a small pre-tilt angle α_0 with the plane of the substrates[4,8]. The various appearances of the figures correspond to different values of α_0.

Pre-tilt angles and influential factors

Using the crystal rotation method, the pre-tilt angle (α_0) of various anti-parallel cells over different rubbing distances was measured. Every cell was tested at eight to ten different places, and the average values of α_0 are summarized in Tab. 1.

Tab. 1. Influence of rubbing distance upon pre-tilt angles

Films	Pre-tilt angle (in degree) at a rubbing distance			
	3 m	6 m	9 m	12 m
P-570	2,0	2,6	3,1	2,5
P3	–[a]	5,8	6,3	–[a]
P11	6,8	8,1	–[a]	–[a]

[a] Difficult to measure due to unsymmetrical curve.

Influence of loading pressure and rubbing distance

A loading pressure of 40 g/cm^2 and a moving distance of 3–12 m were adopted to rub the polymer films. It was found that a uniform orientation of LCs could not be produced under a loading pressure lower than 30 g/cm^2, while a 2 or 20 g/cm^2 load was used to rub a polyimide film[14)], which implies that these polymer films are of higher hardness and crosslinking extent.

The pre-tilt angle α_0 varies with the rubbing distance for all the three polymers (Tab. 1). When the rubbing distance is prolonged from 3 m to 9 m, the α_0 tends to increase. However, if the rubbing distance is too long, i.e. overrubbed, the pre-tilt angle decreases for P-570 and the measurement of the α_0 for P3 and P11 becomes difficult. The measurement of α_0 using the crystal rotation method requires that the LCs between two glass plates form a section of a uniaxial single crystal[2–5,8)]. Therefore, if the uniformity of this single crystal is possibly disturbed by overrubbing, an unsymmetrical curve of the transmittance versus the rotation angle of the cell will result and the α_0 can not be measured. On the other hand, insufficient rubbing (P3 with a rubbing distance of 3 m) fails to align the LCs well enough, and similarly the α_0 becomes unavailable.

Influence of side chains

The pre-tilt angles α_0 of P-570 (2,0–3,1°) are lower than those of P3 (5,8–6,3°) and P11 (6,8–8,1°) (Tab. 1). This is quite reasonable considering that the azobenzene side chains of the ladder-like polysiloxanes (P3 and P11) on substrates induce a homeotropic LC alignment[27,28)], and it is supposed that this homeotropic tendency still functions even after rubbing. So, the overall effect is inducing a higher α_0 of LCs on the P3 and P11 orientation films. According to Tab. 1, the α_0 of P11 is higher than that of P3. This result still coheres with our supposal, since the homeotropic tendency of P11 is stronger than that of P3[28)].

It looks like that the controlling of the pre-tilt angle α_0 is a delicate thing, just as Haaren has mentioned[13)], the selection and processing of these polymers is partly a science and partly a craft, or even an art. However, our results have shown a promising potential of these kinds of polymers, and it is anticipated that we can control and adjust the α_0 by doping with different dosage of homeotropic units.

Stability of the orientation films

We studied the stability of these orientation films by measuring the changes of the pre-tilt angle α_0 before and after annealing at a higher temperature.

A cell using P-570 as the alignment layer and showing a pre-tilt angle of 2,4° was annealed at 100°C for 1–24 h. The relationship between the pre-tilt angles and the annealing time is shown in Fig. 4. The pre-tilt angle decreases to a certain extent at the beginning, which can be probably ascribed to a change of the interaction in the interface betweeen the LC molecules and the surface of the orientation films. After about three hours, the pre-tilt angle tends to be constant.

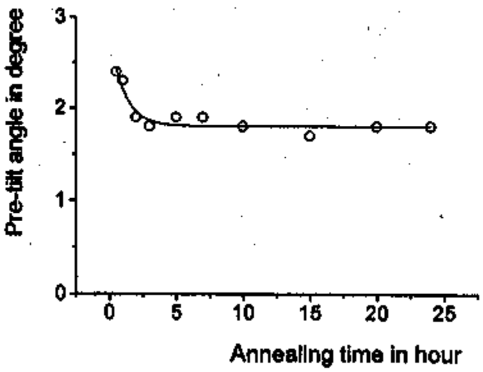


Fig. 4. The pre-tilt angle for P-570 as a function the annealing time at 100°C

Two P11-coated plates, which had been rubbed and then annealed at 180°C for 9 h, were also used to assemble an anti-parallel cell. The unidirectional alignment of this cell was as good as that without annealing. Another homogeneous LC cell which was fabricated half a year ago using rubbed P3 films remained unchanged until now. All of these results demonstrate that the orientation status of these rubbed polymer films is quite stable.

In conclusion, as an orientation medium for liquid crystals, this novel material based on our ladder-like polysiloxanes has shown considerable advantages such as lower curing temperatures (150–200°C), higher pre-tilt angles (2–8°), good stability of the orientation status and so on.

Further studies are underway presently to investigate the physical and chemical properties of these materials, the various factors influencing the pre-tilt angles, the fine control and adjustment of a_0, and to develop its practical application in the LCD field.

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