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RELATIONSHIP BETWEEN MOLECULAR STRUCTURE OF PHOTOSENSITIVE FRAGMENTS AND ALIGNING PROPERTIES OF POLYSILOXANES

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Photoaligning properties of polysiloxanecinnamates layers were investigated. The easy axis direction in a cell plane was found to be dependent upon the position of cinnamate group in side polymer fragments. Both perpendicular and parallel directions of the easy axis with respect to exciting light polarisation were obtained. Presence of the hydrophobic alkyl moieties in the side polymer fragments results in the generation of an oblique alignment of liquid crystal, which is thermostable up to 150°C.

Keywords: Liquid crystals; photoalignment; pretilt angle; polysiloxane

1. INTRODUCTION

Homogeneous aligning of liquid crystals (LCs) is one of the necessary conditions for the normal operation of LC displays. Traditional techniques of rubbing of isotropic polymeric layers do not satisfy the

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increasing demands for alignment quality. Therefore, development of new rubbingless techniques for LC alignment and aligning materials is of great interest during last years [1–4].

One of the new promising aligning techniques is based on the use of photopolymer films [4–12]. Aligning ability of these materials is determined by the anisotropy induced by light illumination. Application of photopolymers allows developing of "clean" contactless method for LC alignment. It permits the control of an easy axis orientation over the aligning surface and the azimuthal anchoring energy value.

Several classes of photoaligning materials have been recently developed and studied [4–12]. Nevertheless a number of important problems are not solved yet. In particular, it concerns thermostability of LC orientation, adhesive properties of aligning layers, possibility of oblique alignment and alignment of some specific LCs, *etc*. Mechanisms of photoalignment have not been investigated enough. Therefore, the search for new photoaligning materials and their investigations are of the current concern.

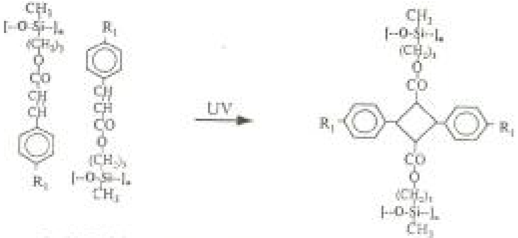
The aim of this article is to investigate the aligning properties of photosensitive polysiloxanes and to establish the relationship between the molecular structure of polysiloxanes and their aligning properties.

Ability of polysiloxane matrices to provide good homogeneous, oblique or homeotropic orientation of nematic LCs is well known [13]. Appending the properties of light-induced anisotropy to these materials is expected to give a combination of good aligning ability of polysiloxane matrices with advantages of photoaligning materials. The first results on aligning properties of such materials were published in our previous article [14]. Here we investigate the relationships between the molecular structure of photosensitive fragments and a character of LC alignment.

2. MATERIALS

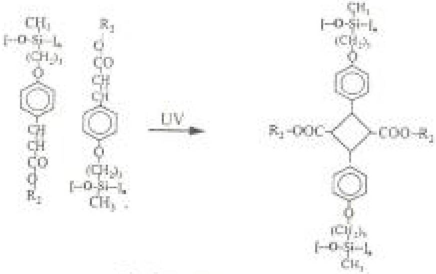
We used esters of cinnamic acid as photosensitive side fragments of polysiloxanes. The synthesized polysiloxanecinnamate aligning materials (PSCN) are presented in the left column of Figure 1. The illumination by UV light initiates the well-known cross-linking

1



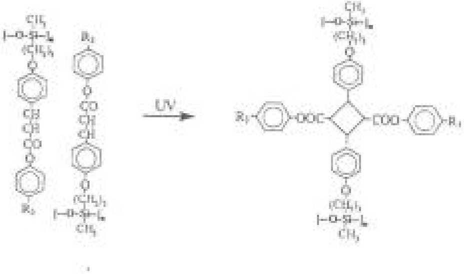
R_1=H, F, OC_3H_7, OC_5H_{11}, OC_7H_{15}, OC_9H_{19}, $OC_{10}H_{21}$

2



R_2=C_2H_5, C_8H_{17}

3



R_3= OCH_3, OC_2H_5, OC_8H_{17}

FIGURE 1 The synthesized and investigated PSCN aligning materials.

reaction [15]. The corresponding photo-products are depicted in the right column of the same figure.

There are three types of synthesized PSCN materials. They differ by stereo-anisotropy of photo-products. The irradiation of the first type results in the appearance of truxillic acid fragments, which determine the stereo-anisotropy axis of the photoproducts to be oriented preferably perpendicular to the parent cinnamoyl side-groups. The materials of the second and the third types give the preferable orientation of truxillic acid fragments and stereo-anisotropy axis parallel to the parent cinnamic side-groups. Specific feature of the third type materials is a "cross"-like structure of photo-products, and it is difficult to determine the direction of stereo-anisotropy axis.

The PSCN of the first type was obtained by heating of alkyl 4-(alkoxy, fluoro)- or unsubstituted cinnamates and trichlorosilane in the presence of hexachloroplatinic acid followed by the hydrolysis of corresponding 3-cinnamoyloxypropyltrichlorosilanes.

The PSCN of the second and third types were obtained from alkyl or aryl esters of the 4-allyloxycinnamic acid and methylpolysiloxane in boiling toluene in presence of hexachloroplatinic acid as a catalyst. The resulting PSCN was extracted by diluting a reaction mixture with methanol and filtering the reaction products, drying in vacuum and then crushing in a vibrating mill.

Two groups of commercial nematic LCs were used in experiments. One group includes the mixtures ZLI 4801-000 and ZLI 4801-100 (Merck, Korea), which are used in active-matrix LC display devices. The other group includes pentyl-cyanobiphenyl (NIOPIK, Russia) and the mixtures of cyanobiphenyls and esters of benzoic acids: E7 (Merck, Germany), ZhKM-1282 and ZhKM-1285 (NIOPIK, Russia), which are used in simple twist indicators.

3. METHOD

For the preparation of aligning surfaces the solution of polysiloxane in chlorobenzene was made. We spread out the solution onto glass substrates by spin coating (4000 rev/min) for 30 s. As a result, a thin polymer film (less then 0.1 μm) was created on a glass substrate. Then substrates were annealed under high temperature (150°C, 1 hour).

Substrates with polymer films were illuminated by polarized UV-light of a high-pressure mercury lamp. The main spectral lines of the lamp corresponded to the absorption band of photosiloxanes. A light beam with polarization vector $\boldsymbol{E}_{uv}$ in the plane of the polymer film was formed by a quartz lens system and a polarizing Glann-Thomson prism. The typical value of light intensity, I_O, in the plane of a polymer film was 5 – 10 mW/cm^2. The exposure time t_{exp} was 10 min.

After UV light illumination LC cells were assembled with the gap given by teflon strips of 30 μm thickness. Cells were filled by the capillary effect at room temperature with liquid crystal being in the nematic phase.

Two types of cells were made. The first one (symmetric cell) consisted of two similar substrates covered with polysiloxane film; cells of the second type (combined cell) were composed of a substrate covered with polysiloxane film and a substrate covered with rubbed polyimide film. The rubbed surface was used as a reference surface. The pretilt angle, $\theta_{ref} \approx 5^\circ$ (an angle between easy orientation axis of LC and aligning surface) on the rubbed surface was given by the direction and strength of rubbing and was independent of the direction of LC filling.

Symmetric cells were examined for the aligning ability of polysiloxane films. The general characteristics of LC orientation were determined under a polarizing microscope (Model LOMO-R211). The direction of the director, $\mathbf{d}$, in the cell was determined by a light scattering technique [10].

We used the combined cell to measure the pretilt angle, θ_{test}, on the tested polysiloxane surface [16, 17]. One can calculate the value of the pretilt angle on the tested surface θ_{test} from the measured value of the average pretilt angle over the cell, $\overline{\theta}$.

The average pretilt angle $\overline{\theta}$ was measured by a well known crystal rotation technique. A cell was placed between crossed polarizers so that the director made angle 45° with their axes. Then the cell was rotated around the axis perpendicular to the director. The dependence of the system transparency $T(\phi)$ for a probe He – Ne laser beam on the angle, ϕ, between the beam and the cell normal was measured. The value of $\overline{\theta}$ was given by the expression

$$\overline{\theta} \approx \frac{\Delta\phi}{(n_e + n_o)} \approx \frac{\theta_{ref} + \theta_{test}}{2} \tag{1}$$

Here $\Delta\phi$ is the shift of the symmetry axis of the curve $T(\phi)$ from the point $\phi = 0$, n_o, n_e are the refractive indices for the ordinary and extraordinary light waves, respectively. In our experiments the combined cell was filled along the direction of rubbing. It should provide the reverse oblique distribution of director in the cell [15, 16]. For this geometry the value θ_{test} in (1) has the opposite sign to θ_{ref}.

4. EXPERIMENT AND DISCUSSION

Investigations of symmetric cells under the polarizing microscope showed the unidirectional alignment of LC for all studied aligning materials. All liquid crystals containing cyanobiphenyl molecules were oriented homeotropically on all PSCN materials. The excellent quality of the thermostable alignment was achieved. We did not find any degradation of alignment quality after keeping the cells at 200°C during several hours.

PSCN polymers provided a high quality homogeneous alignment of ZLI 4801-000 and ZLI 4801-100 LC mixtures. The determination of the direction *d* by scattering technique in symmetric cells showed perpendicular direction of vector *d* to vector E_{uv} for the materials of the first and third types (see Fig. 1), while *d* and E_{uv} were parallel to each other for materials of the second type. This observation was confirmed by the results obtained with combined cells: the cells with ening materials of the first and third types manifested usual planar structure while excellent $(90 \pm 2)°$ – twist structures were obtained in the cells with materials of the second type.

The parallelism of the direction of the light induced easy axis and the LC director on the tested surfaces points to the strong anchoring of LC on the polysiloxane surface. It means that anchoring parameter $\xi = W_{test} L/K \gg 1$ (W_{test} is anchoring energy, K is a Frank constant) [18]. For the typical values $K = 5 \cdot 10^{-7}$ dyne and $L = 30\,\mu m$ one get the estimated value of $W_{test} \geq 10^{-2}\,erg\,cm^{-2}$.

Alignment in all cells did not change even when the cells are kept in nematic phase right below the clearing point, T_c, for several days. Overheating symmetric cells above T_c and keeping under temperature $T \approx 150°C$ followed by cooling did not lead to total destruction of alignment, but few disclinations appeared at the polymer surfaces. The same treatment of combined cells did not cause appearance of any defects.

The observed surface defects might be associated with the presence of domains that have different signs of the pretilt angle on the surface.

The occurrence of such types of domains seemed to be a charateristic feature of photo-orientants. Indeed, the direction of the easy axis is double degenerated on the photosensitive polymers [17]. These results are consistent with the absence of surface defects in the combined cells, where strong anchoring at the rubbed surface prevents their appearance.

We showed the oblique LC alignment on polysiloxane surfaces by the direct measurements of the pretilt angle in the combined cells. The pretilt angle was found to be essentially dependent on the length of the aliphatic tail in a side chain of the polymer. Orientants with shorter tails (R = H, F, C_2H_5, OCH_3, OC_2H_5, OC_3H_7, OC_5H_{11}, OC_7H_{15}) induced negligibly small pretilt angle. In the case of longer tails (R = C_8H_{17}, OC_8H_{17}, OC_9H_{19}, $OC_{10}H_{21}$) a sufficient pretilt angle occurred that increased nonlinearly with increasing tail length. It was noticed that materials with too long tails manifest poor aligning ability. The dependence of the pretilt angle value on number n of the aliphatic groups (C_nH_{2n+1}) for orientants of type I is presented in Figure 2. The dependence of the pretilt angle on the length of the aliphatic fragments is essentially nonlinear. While reproducibility and

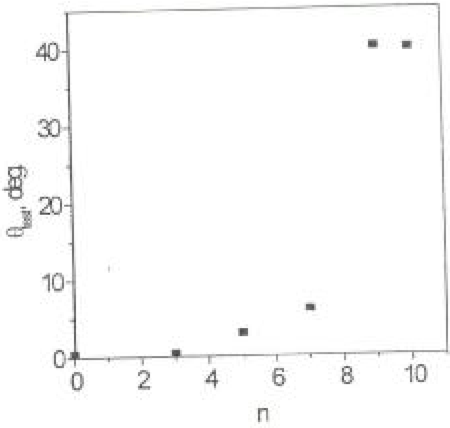


FIGURE 2 The dependence of the pretilt angle value on the number, n, of groups C_nH_{2n+1} for orientants of type 1.

stability of the pretilt angles of low and high magnitudes are good, the intermediate values are not well reproducible.

Contrary to polyvinyl-cinnamates and their derivatives, the pretilt angle on polysiloxane surfaces turns out to be constant in time. We did not find significant changes of the pretilt angle for a half of year. Moreover, the pretilt angle did not change after keeping cells at temperature $T = 150°C$ for 4 hours.

The presented results may be discussed in terms of the stereo-anisotropy and electron properties of the initial photosensitive fragments of polysiloxanes and their photo-products.

The geometric and electronic structure of the virgin side-chain fragments is strongly anisotropic. Howeover, since these fragments are initially oriented at random, the non-irradiated polysiloxane surface is isotropic and there is no preferable direction for LC molecules.

The side-groups of polysiloxanes exhibit a strong positive dichroism of the UV light absorption [9, 15]. Therefore, the side-groups which are oriented along vector E_{uv} absorb light most effectively. As a result, on the irradiated polymer surface, the anisotropic distribution appears of both the side-groups and the cross-linked bonds. It leads to appearance of an easy axis for LC orientation. Direction of the easy axis depends on peculiarities of the orientational interaction between LC molecules and polymer surface.

The materials of the first group are similar to the well-known polyvinylcinnamate aligning polymers [9, 10], where polyvinyl main chain is substituted with the siloxane one. As in the case of polyvinylcinnamates, the axis of stereo-anisotropy of photo-products is determined by the long axes of the truxillic acid bridges. It is lined up perpendicular to the parent cinnamoyl fragments and to vector E_{uv}. The orientational interaction between LC and polymer molecules is determined by the dispersive and steric forces [17], which are stronger along the long axes of the truxillic acid bridges. Consequently, the vector of the easy axis e has to be perpendicular to E_{uv}, as was found out for polysiloxanes of the first group and for the known PVCNs [9 – 10], as well.

The action of UV light on the materials of the second group induces the stereo-anisotropy axis, which is parallel to E_{uv}. As a result, the direction of e is parallel to E_{uv}. It should be noted, that the coincidence of the directions of d and E_{uv} is quite unusual. In studied systems

[4–12], light-induced direction *d* is always perpendicular to the polarization of exciting light and only one communication [19] is known where *d* and E_{uv} coincide in a rather exotic system.

The UV light illumination of materials of the third group causes the generation of the cross-like fragments between the main chains. In this case, two stereo-anisotropy axes associated with two cross-bars may be found. Longitudinal cross-bars formed by the truxillic acid fragments connect the main polymer chains and are parallel to vector E_{uv}. Lateral cross-bars are perpendicular to E_{uv} and are not connected directly with the main chains. Now, a direction of easy axis *e* is determined by competition between the orientational abilities of the two cross-bars and was found to be perpendicular to polarization E_{uv}. This fact may be explained by the main contribution of the dispersion forces to the LC alignment. Actually, the π-conjugation of the electron system is more effective in the lateral cross-bars involving COO-group connected with phenyl ring.

5. CONCLUSIONS

1. Polymers on the base of polysiloxanes containing photosensitive cinnamoyl side chain fragments can provide the thermostable and uniform homogeneous alignment of nematic LC induced by the polarized UV light.
2. Direction of an easy axis *e* on the PSCN surface corresponds to the direction of polarization E_{uv} of UV light and is determined by the stereo-anisotropy of photo-products. Direction of vector *e* can be either parallel or perpendicular to vector E_{uv}.
3. Presence of the hydrophobic alkyl chains leads to generation of an oblique alignment of a liquid crystal, which is stable at least up to temperature 150°C.

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