

# Factors in liquid crystal photoalignment on polymer films: photoorientation versus self-assembly

O. YAROSHCHUK†,‡, V. CHIGRINOV‡, O. NADTOKA§ and H. KWOK‡

 †Institute of Physics, NASU, Prospect Nauki, 46, 03028 Kyiv, Ukraine
 ‡Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China §Kyiv National Taras Shevchenko University, Volodymyrs'ka St., 64, 01033 Kyiv, Ukraine

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We demonstrate that photostimulated self-assembly, running in parallel with molecular photoorientation in the top layer of the aligning polymer film, breaks the bulk molecular order mainly determined by the symmetry of irradiation. This may substantially modify liquid crystal (LC) alignment. Depending on the chemical composition of the liquid crystal, the self-assembled layers may influence either homeotropic or planar LC alignment with extremely weak azimuthal anchoring. Effective self-assembly occurs in polymers having side chain chromophores with flexible spacers and polar terminal groups.

## 1. Introduction

The ability of photochromic materials to become anisotropic under irradiation with polarized light, known as the Weigert effect [1], is of great interest in technologies for information storage, processing and transfer [2], as well as in the manufacture of passive optical elements [3, 4]. Moreover, in the past decade, the ability of the films with a photoinduced anisotropy to align liquid crystals (LCs) was discovered, a phenomenon usually known as photoalignment. First Ichimura et al. [5], using chemically adsorbed layers of azobenzene derivatives, demonstrated homeotropic/planar alignment transition governed by unpolarized actinic light. Later, Gibbons et al. [6] obtained uniform planar alignment of a LC on azopolymer films treated with polarized light. Recently, utilizing a similar treatment procedure, Chigrinov et al. [7] observed highly uniform planar/tilted LC alignment on azodye films physically adsorbed on glass/ITO substrates. This photoalignment process was extended to a class of photocrosslinkable polymers, allowing the achievement of LC alignment with improved thermal stability and photostability [8, 9].

Currently, photoalignment attracts great attention as a most promising candidate to replace the traditional rubbing technique in the new generation of LC displays. In avoiding direct mechanical contact with the aligning substrate, photoalignment is free of the principal drawbacks of rubbing, such as surface deterioration, electrostatic charge generation and dust formation. In addition, this procedure permits the smooth control of anchoring energy and LC pretilt angle, and the ready formation of patterned LC alignment.

The alignment of a liquid crystal on a photoirradiated polymer substrate is usually explained by anisotropic molecular interaction at the LC/substrate interface. Dispersive, polar and steric interactions contribute to this alignment mechanism. In some situations, e.g. in the case of LC alignment on holographic gratings, anisotropic surface topology may also be an important alignment factor [10, 11].

According to this mechanism, uniform photoalignment of a liquid crystal is a result of uniform alignment of polymer fragments and their photoproducts with actinic light. Molecular ordering under irradiation strongly depends on the prevalent photochemistry of the photosensitive fragments. In the case of azopolymers, the ordering features are determined by the parameters of trans-cis isomerization of azofragments. The angular selection or reorientation of transazochromophores perpendicular to the polarization direction of the actinic light, E<sub>a</sub>, may prevail depending on the lifetime of *cis*-chromophores and the spectral composition of the actinic light [12]. Angular selection of chromophores resulting in their alignment perpendicular to  $E_a$ , is considered to be a major photoordering process in the case of crosslinking polymers [8, 9, 13] and photosensitive polyimides [14, 15], because of the strong stability of the corresponding photoproducts.

It is important to note that the orientational order of chromophores determined by the geometry of light irradiation may be substantially modified by the light

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<sup>\*</sup>Corresponding author. Email: olegyar@iop.kiev.ua

stimulated processes of self-organization, especially in polymer homologues with liquid crystalline properties. The superposition of metastable photoinduced order (determined by the geometry of the light field) and thermodynamic order (determined by intrinsic molecular self-organization) may result in a strong enhancement of the ordering parameter as well as in an alignment configuration far from that determined by the light symmetry [16, 17]. Self-organization processes are especially strong at elevated temperatures close to the temperature of polymer solidification (glass transition temperature  $T_{\rm g}$ , or crystallization temperature  $T_{\rm Cr}$ ) [18, 19]. However, they can be significant even at ambient temperatures in polymers with a low temperature of solidification, when subjected to UV irradiation [16, 17].

Self-organization processes under irradiation may be active in the bulk and also on the surface of polymer films. However, the bulk and surface orders formed under irradiation may be substantially different. In previous work we revealed this discrepancy in the study of two azopolymers [20]. One of them, having a high  $T_{\rm g}$ , demonstrated similar ordering of azochromophores in the bulk and on the polymer surface. The alignment of azochromophores at the polymer surface and the alignment of LC contacting with this polymer were controlled by the direction of irradiation. The other polymer, with a low temperature of solidification, demonstrated controllable photoinduced order in the polymer bulk, while alignment of surface azochromophores was homeotropic and not controllable by the action of light. Films of this polymer led to homeotropic LC alignment independent of the irradiation conditions. According to our prior assumption [20], photoirradiation of polymers having a low temperature of solidification stimulates the self-organization of azochromophores in the form of self-assembly. The upright order formed in this process is guite strong and resistant to the action of light. This assumption about light-induced self-assembly of azochromophores should, of course, be proved and the conditions of this process should be more deeply studied.

In the present paper, light-induced self-assembly in the top layers of azopolymer films is discussed, comparing LC alignment on films subjected to baking  $(T>T_g)$  and irradiation. The role of self-assembly in LC alignment is studied for a large number of azopolymers from different chemical classes. It is established that effective self-assembly occurs in polymers having side chain chromopores with flexible spacers and polar terminal groups, regardless of the temperature of solidification. It is also shown that the type of LC alignment on self-assembled layers of azochromophores depends on the chemical composition of the LC. For cyanobiphenyl-containing LC mixtures homeotropic alignment is typically realized. At the same time, for an active matrix LC mixture we observed planar LC alignment with extremely weak azimuthal anchoring. It is additionally ascertained that the self-assembly process hampers tilted alignment and pretilt angle control. This clearly demonstrates the important role of self-assembly in liquid crystal photoalignment with polymer films, which cannot be ignored in industrial processing.

## 2. Experimental

## 2.1. Aligning materials

We used two series of azopolymers: (i) azopolymalonates differing in the terminal substitution in the azochromophores, figure 1(a), and (ii) azopolymethacrylates having different terminal substitutions and side chain spacers, figure 1(b). The preparation of these compounds was described previously in [21] and [22], respectively.

The phase transitions of the polymers were studied by polarizing optical microscopy and differential scanning calorimetry. The phase transition temperatures are presented in table 1. It can be seen that polymers P1– P3 from the azopolymalonate series show low temperatures of solidification, while azopolymethacrylates P4 and P5 retain a glassy state up to 113 and 112°C, respectively. The latter polymer also possesses liquid cryslalline properties in the temperature range 112– 140°C.

## 2.2. Films

Polymer films were prepared by spin coating of polymer solution onto glass or glass/ITO slides. For this purpose the polymalonates were dissolved in dichloroethane, and the methacrylic polymers in dimethylformamide. The weight concentration of polymers in these solutions was about 2%; the spin velocity was 2 500 rpm. The coated films were baked at 90°C for 1 h to complete solvent evaporation. After the baking procedure the substrates were cooled to ambient temperature at a rate of about 5°C min<sup>-1</sup>.

To induce anisotropy and LC alignment ability, the films were irradiated obliquely with a beam of nonpolarized UV light ( $\lambda_{ex}$ =365 nm) from a mercury lamp. The light intensity was about 8 mW cm<sup>-2</sup>. The light incidence angle  $\alpha$ , from the film normal, was varied in the range 0°–70°. Additionally, for the purpose of tilted homogeneous LC alignment, we used a standard twostep irradiation [23–25]: first with polarized UV light (3.5 mW cm<sup>-2</sup>, 10 min) and then with non-polarized UV



P<sub>4</sub>: R=NO<sub>2</sub>, m=2 P<sub>5</sub>: R= OC<sub>4</sub>H<sub>9</sub>, m=6

Figure 1. Chemical structures of azopolymers: (a) azopolymalonates; (b) azopolymethacrylates.

light  $(8 \text{ mW cm}^{-2}, 2 \text{ min})$  by sample rotation of  $90^{\circ}$  around its normal. Both irradiations were carried out obliquely ( $\alpha$ =45°). The second irradiation step was needed to break the two-fold degeneration of LC tilt arising after the polarized light irradiation.

# 2.3. LC cells

Each LC cell was constructed by sandwiching the LC between a pair of glass/ITO substrates coated with azopolymer and irradiated as described above. To obtain a uniform director orientation across the cells, they were assembled in an antiparallel fashion, the substrates being set so that the vectors specifying the direction of irradiation with non-polarized light were antiparallel to each other. Cell thickness was adjusted by spacers with a diameter of  $20 \,\mu\text{m}$ . These cells, termed

Table 1. Characteristics of azopolymers. Cr, g and I denote, respectively, crystalline, glassy and isotropic phases; N and SmA denote, respectively, nematic and smectic A mesophases.

Polymer	Transition temperatures/°C	$M_{\rm p}$ , g mol <sup>-1</sup>
P1	Cr <sub>1</sub> 32 Cr <sub>2</sub> 44 SmA 52 N 55 I	7000
P2	g 7 C 58 N 62 I	7519
P3	Cr 63 N 75 I	5820
P4	g 113 I	38000
P5	g 112 SmA 140	47000

symmetrical cells by us, were used to determine the type of LC alignment (homeotropic, planar or tilted), and also to measure pretilt angle and polar anchoring energy.

For the azimuthal energy tests we also constructed cells consisting of one rubbed polyimide substrate and a photoaligned azopolymer substrate (asymmetrical cells). The easy axis of the azopolymer substrate was turned  $90^{\circ}$  with respect to the rubbing direction of the polyimide substrate.

The cells were filled under room conditions with different kinds of nematic LC: K15, E70, MLC5700-000, MLC12100-000 and MLC 6610, all from Merck. The K15, E70 and MLC5700-000 LC, used for TN and STN displays, mainly consist of cyanobiphenyl (CB) derivatives. The MLC12100-000 was developed for active matrix LCDs. These mixtures, along with cyanobiphenyls, also contain tolane and phenylcyclohexane derivatives. The MLC 6610 composition serves for VAN LCD; it contains molecules with a dipole moment oriented perpendicularly to the molecular long axis, providing negative dielectric anisotropy.

#### 2.4. Anisotropy testing in the azopolymer films

The recording and degradation of the photoinduced anisotropy in azopolymer films were studied by the transmission null ellipsometry method previously validated for this purpose [16, 17, 26]. This method yields the in-plane and out-of-plane film retardation for different irradiation doses as well as the alignment direction(s) of azochromophores. Specifically, in the case of oblique irradiation with non-polarized light (which commonly leads to uniaxial alignment of azochromophores in the direction of light propagation in the polymer), this method produces the tilt angle of the azochromophore alignment axis and a phase retardation ( $n_e$ - $n_o$ )d, where  $n_e$  and  $n_o$  are extraordinary and ordinary refractive indices, respectively, and d is the thickness of the polymer film. The phase retardation is coupled with the azochromophore order parameter [7].

## 2.5. Alignment testing methods

The LC alignment was first observed visually by placing samples between a pair of crossed polarizers in the polarizing microscope. The LC pretilt angle was measured by a crystal rotation method described elsewhere [27]. The pretilt angle was determined by fitting theoretical curves to the experimentally measured plot of transmittance as a function of the incidence angle of the He-Ne laser beam used as probing light. The polar anchoring energy was measured by modified Yokoyama and van Sprang method [28]. The azimuthal anchoring was determined from the twist angle measurement in the asymmetric cells [7].

# 3. Results and discussion

The results of LC alignment are presented in table 2. It can be seen that oblique irradiation with nonpolarized light induces homeotropic alignment of the cyanobiphenyl-based LCs (K15, E70 and MLC5700-000) on films of polymers P1–P4. This alignment is unaffected by the incidence angle  $\alpha$  of the UV light. The other two liquid crystals show random planar alignment with a pronounced flowing effect. Polymer P5 causes homeotropic or tilted LC alignment depending on whether  $\alpha = 0^{\circ}$  or  $\alpha \neq 0^{\circ}$ , respectively. Surprisingly, the alignment characteristics on P5 films are similar for all the liquid crystals used, independent of their chemical composition.

The described photoalignment properties occur over a range of irradiation dose. On the one hand, the initiation of homeotropic or tilted alignment requires a dosage of about  $0.1 \,\mathrm{J}\,\mathrm{cm}^{-2}$ ; on the other, homeotropic/ tilted alignment degrades at high irradiation doses. Figure 2 shows photographs of two symmetric LC cells, based on (*a*) P1 and (*b*) P3 alignment layers, viewed between crossed polarizers. Sections 1, 2 and 3 of the aligning substrates were exposed, respectively, to doses 0, 7.2 and 33.6 J cm<sup>-2</sup>. It can be seen that extended irradiation results in the degradation of homeotropic alignment and causes a transition to random planar alignment.

To elucidate the reasons for homeotropic/tilted alignment and its degradation at high irradiation doses, we studied the photoordering kinetics of azochromophores in the film bulk by means of transmission null ellipsometry. According to the results obtained, nonpolarized light induces uniaxial alignment of azochromophores towards the incidence direction of the UV light (in a polymer medium). The azochromophore alignment direction can be steered by the direction of the UV irradiation, but not with the irradiation dose. In contrast, photoinduced birefringence is a function of

Table 2. The results of liquid crystal alignment on the studied azopolymers. The symbols h, p and n/a denote homeotropic, planar and no alignment, respectively.

	Liquid Crystal					
Polymer	5CB (K15)	E70	MLC 5700-000	MLC 12100-000	MLC 6610	
Irradiation with n	on-polarized UV light					
P1	h	h	h	p (random)	p (random)	
P2	h	h	h	h	p (random)	
P3	h	h	h	h	ĥ	
P4	h	h	h	p (random)	p (random)	
P5	h/tilted	h/tilted	h/tilted	h/tilted	h/tilted	
Irradiation with p	oolarized UV light					
P1	n/a	n/a	n/a	p (highly uniform)	p (uniform)	
P2	h	h	h	p (uniform)	n/a	
P3	h	h	h	h	h	
P4	h	h	h	n/a	n/a	
P5	tilt/h	tilt/h	tilt/h	tilt/h	tilt/h	

irradiation dose. The latter function for a P3 film is presented in figure 3. It corresponds to a light incidence angle of  $\alpha = 45^{\circ}$ , which leads the azochromophore ordering axis to be tilted  $10^{\circ}$  from the film normal. Birefringence grows with the irradiation dose, passes through a maximum and then decreases, approaching zero which corresponds to a spatially isotropic state of the film. The numbers 1, 2 and 3 in figure 3 denote irradiation doses corresponding to the cell sections 1, 2 and 3 in figure 2. Comparing figures 2 and 3 one can conclude that approximately the same irradiation dose is needed to destroy azochromophore ordering in the bulk (coupled with film anisotropy) and on the surface of the polymer film (coupled with LC alignment). This is not surprising, since the polymer film is thin, and light intensity across the film is quite uniform. The most probable reason for the alignment deterioration is a





Figure 2. Photographs of two symmetric cells filled with LC K15 viewed between crossed polarizers: (*a*) (on-axis view of cell, (*b*) off-axis view of cell. Cell (*a*) contains P1 aligning films, while the cell (*b*) contains P3 aligning films. The films were obliquely treated with non-polarized UV light at an incidence angle of  $45^{\circ}$ . The irradiation time was 0, 15 and 70 min in cell sections 1, 2 and 3, respectively.

photodestruction of azochromophores, which should be taken into account at high irradiation doses.

The photoordering behaviour of azochromophores described for polymer P3 is common for all the azopolymers under investigation. This particularly means that azochromophores in all the polymers align towards the direction of light propagation, and so their alignment direction can be steered by the incidence direction of the actinic light. Correspondingly, LC alignment direction should be controllable according to the alignment model discussed above. This is true for P5, but not for P1-P4 aligning films. As we supposed in [20], the latter might be caused by differences in the surface and bulk ordering of azochromophores. The reason for this difference may be self-assembly at the film/air interface leading to the upright ordering of azochromophores. The self-assembly, as with the selforganization in a bulk polymer, can be stimulated by UV light, but the ordering direction is not determined by the direction of light irradiation. In the case of P1 films, this assumption is consistent with the results of Xray reflectivity, which shows no change in the orientation of surface azochromophores with changing incidence angle of the UV light [20]. The upright ordering at a polymer surface created by a self-assembly of azochromophores may cause homeotropic LC alignment, insensitive to the angle of UV light incidence.

Thus, according to the suggested alignment mechanism, the photoinduced homeotropic alignment of a cyanobiphenyl LC on P1–P4 films is a result of the light-stimulated self-assembly of azochromophores. This assumption needs to be additionally proved. If surface alignment of azochromophores is a self-assembly process (i.e. a thermodynamic process leading to minimization of surface free energy), it should also



Figure 3. Plot of birefringence versus exposure time for polymer P3, involving oblique irradiation with non-polarized UV light ( $I=8 \text{ mW cm}^{-2}$ ,  $\alpha=45^{\circ}$ ). The irradiation causes uniaxial anisotropy with the optic axis tilted 12° with respect to the film normal. The numbers 1, 2 and 3 mark irradiation doses corresponding to the cell sections 1, 2 and 3 in figure 2.

be thermally activated. To check this possibility, P1 and P3 films were heated to 100°C, corresponding to the isotropic state (see table 1), and then slowly  $(\leq 0.5^{\circ} \text{ min}^{-1})$  cooled to room temperature. The LC cells based on these substrates indeed showed homeotropic alignment of a cyanobiphenyl-based LC, reflecting upright order of the azochromophores. The slow cooling rate was an indispensable condition for homeotropic alignment: neither baked films rapidly cooled, nor non-backed films, showed any type of uniform LC alignment. We believe that a self-assembled layer of azochromophores formed at  $T>T_c$  is 'frozen' by slow cooling of the polymer film below the temperature of solidification; fast cooling destroys this layer. It is noteworthy that thermally induced homeotropic alignment is less stable than the alignment induced by actinic light (figure 4). Presumably, the

bulk ordering of azochromophores in photoalignment stabilizes the self-assembly order at the polymer surface. In turn, spatially random alignment in baked polymer films, established by the ellipsometry method, gradually destroys the surface ordering of azochromophores. These results imply coupling between the bulk and surface ordering of azochromophores.

As mentioned in the Introduction, we previously observed effective light-induced self-organization in polymers with low temperatures of solidification, particularly in the polymers P1–P3 presently used for photoalignment [17]. It is reasonable that bulk self-organization in these polymers may be accompanied by self-assembly at the polymer surface, which is a process of surface self-organization. However, *prima facie*, self-assembly on films of methacrylic polymer P4, indicated by homeotropic LC alignment, looks strange. In reality,



Figure 4. Scheme demonstrating the procedures of homeotropic LC alignment and the stability of these alignments with age. The LC cells placed between crossed polarizers are viewed in the normal direction. UV indicates a photoalignment treatment of the bounding substrates before the cell assembly; t° indicates a tempering procedure of the filled cells (heating to  $100^{\circ}$ C and subsequent cooling to room temperature).

polymer P4 has a high glass transition temperature which, according to [29], causes weak self-organization of deeply 'frozen' azochromophores in the bulk polymer under UV irradiation. The results for P4 show that, in contrast to the bulk, surface self-organization under UV light can be effective even for polymers with a high temperature of solidification. This may be caused by large 'free volume' [30] at the polymer border and a strong tendency for self-organization of the polar azochromophores. Indeed, because of the NO<sub>2</sub> terminal group, azochromophores in polymer P4 are strongly polarized (push-pull chromophores), having a dipole moment approximately parallel to the molecular long axis of the rod-like chromophores. Because of the dipole-dipole interaction, these chromophores tend to align parallel to each other. This self-ordering process can be realized because the flexible connection between the backbones and azochromophores gives rotational freedom to the latter fragments. In this process the dipole moments usually point normally to the polymer/ air interface (upright ordering) [31].

A high polarity of the azochromophores seems to be an indispensable condition of self-assembly in polymers with a high temperature of solidification. This is evident if one compares the LC alignment on P4 and P5 films: while the homeotropic alignment on P4 films is photoresistant, the LC easy axis on P5 films can be governed by the light. The latter is possible because the self-assembly of non-polar azochromophores (P5 polymer) is much weaker than that of the polar azochromophores (polymer P4). Due to the weak self-assembly, surface order on the P5 films is determined by the light symmetry, as in the bulk polymer. Thus azochromophores are tilted towards the beam of the non-polarized light that determines the LC tilt direction. This process breaks the conical degeneration of the LC easy axis on the non-irradiated substrate, with the angle between the cone generatrix and substrate equal to the pretilt angle. The value of the pretilt angle is a complex function of polymer and LC structure which determine LCpolymer interaction.

Let us now consider the dominant types of interfacial interaction. We believe that the dipole–dipole interaction of azochromophores and LC molecules is a very important factor in the LC alignment on self-assembled azochromophore layers, and may be decisive in the case of polar LC molecules (cyanobiphenyl-based LC) and polar azochromophores (P1 and P4 polymers). Due to dipole–dipole interaction, the dipole moments of azochromophores and LC molecules tend to be parallel. In the case of cyanobiphenyl-based LC molecules, having a strong dipole moment along the molecular long axis, the parallel alignment of dipoles should result in homeotropic LC alignment. In contrast, the nematic mixture MLC 6610, having molecules with a transverse dipole moment, should show planar alignment. These expectations fully correspond to our experimental observations. Interestingly, a similar difference in the alignment of LCs with positive and negative dielectric anisotropy was earlier observed for  $SiO_x$  alignment layers. This was also explained assuming a dominant role of the dipole–dipole interactions at the LC/SiO<sub>x</sub> interface [32].

The random planar alignment of the active matrix mixture MLC12100-000 on P1 and P4 films can also be explained within the scope of the present model. Indeed, the major components of this LC mixture are only weakly polarized along the molecular long axis, which diminishes the role of the dipole–dipole interactions and thus weakens tendency to homeotropic LC alignment.

A strong capability of polymers P2 and P3 to align LC homeotropically may be explained by the alkyl terminal groups making the alignment substrates hydrophobic. The insensitivity of LC alignment to the exposure angle might suggest a self-assembly of azochromophores under irradiation. The weak dependence of LC alignment on the type of LC material may be evidence of weak dipole–dipole interfacial interactions. This type of interaction also plays a secondary role in the alignment of all LC types. Thus, in the case of azochromophores with long hydrophobic tails, dispersion and steric factors of interfacial interaction should dominate.

Finally, we discuss LC alignment obtained by the combination of polarized and non-polarized light. In contrast to the result obtained with only non-polarized irradiation, homeotropic alignment of a cyanobiphenylbased LC is not realized on P1 films. Instead, the combination of polarized and non-polarized light causes the nucleation of LC alignment with a high pretilt angle in the alignment domains. This may imply that the self-assembled layer on top of the P1 films is damaged. At the same time, the two-step irradiation procedure allows us to realize a highly uniform alignment of the active matrix mixture MLC12100-000. In trying to estimate the azimuthal anchoring in these cells, we observed that the azimuthal anchoring strength  $W_{\rm a}$  is extremely small and the LC practically glides on the aligning substrate. This makes the P1 material rather promising for the gliding LCD mode recently suggested [33]. The mixture MLC6610 on P1 substrates also shows planar alignment with a weak azimuthal anchoring.

Similarly to the non-polarized irradiation described above, two-step irradiation causes homeotropic

alignment on P2–P4 films and homeotropic/tilted alignment on P5 films. In the latter case the LC pretilt angle is controllable. Figure 5 shows that the pretilt angle can be varied in a wide range with the angle of incidence of the non-polarized light (second step irradiation). This alignment is characterized by weak azimuthal and polar anchoring; in the case of LC MLC5700-000, the anchoring strength coefficients  $W_{\rm a}$  and  $W_{\rm p}$  are estimated to be  $7 \times 10^{-7}$  and  $8.0 \times 10^{-5}$  J m<sup>-2</sup>, respectively.

## 4. Conclusions

Our results demonstrate that light-stimulated selfassembly processes in a top polymer layer may substantially modify LC alignment influenced by molecular photoorientation, in turn determined by the light symmetry. In some experimental cases the process of surface self-organization may totally suppress the photoorientation of the molecular units, which is assumed to be the major factor of LC photoalignment. Light-induced self-assembly at the polymer surface is characterized by upright order, which induces homeotropic LC alignment. This is a new mechanism of homeotropic LC photoalignment. In contrast to the known mechanism of Ichimura et al. [5] based on molecular photochemistry, the new mechanism involves intrinsic molecular self-organization. Thus the role of the actinic light is reduced to the stimulation of molecular motions that accelerate bulk and surface molecular self-organization. The bulk and surface order of irradiated films are rather similar in the case of weak self-assembly. In the opposite case, they can be



Figure 5. LC pretilt angle versus exposure angle plots for P5 substrates. The squares and triangles correspond to K15 and MLC12100-000 LC, respectively. Two-step oblique irradiation (polarized UV light,  $3.5 \text{ mW cm}^{-2}$ , 10 min) followed by non-polarized UV light ( $8 \text{ mW cm}^{-2}$ , 2 min) was used. After the first irradiation step, the substrate was rotated 90° around its normal to follow the alignment direction induced by the polarized light.

substantially different. While bulk self-organization is effective only in polymers with a low temperature of solidification, surface self-assembly under irradiation can also be strong in polymers with high  $T_c$ ; for example, in polymers containing azochromophores with polar terminal groups on one side and flexible spacers on the other.

Self-assembly should be suppressed to obtain command substrates for LC alignment. This is realized in the case of P5 films. Because of the wide range of pretilt angles, this polymer and its analogues are attractive for VA [34], bistable [35] and other LCD modes. On the other hand, polymer films containing self-assembled layers on the top are also attractive for LCD applications. First, as we demonstrated, the self-assembled layers may cause extremely low azimuthal anchoring, which is probably needed to realize the gliding LCD mode recently suggested [33]. In addition self-assembled layers can be used for stable homeotropic LC alignment, especially in case of cyanobiphenyl-based LC mixtures.

According to Kawatsuki *et al.* [36], self-organization processes substantially influence the photoalignment in cinnamate-containing polymers. This is a reason to believe that the rules obtained for azopolymers are also applicable to the other classes of photosensitive polymers used for LC photoalignment.

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