The Factors of Liquid Crystal Photoalignment on Polymer Films: Photoorientation versus Self-Assembling

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ABSTRACT

The liquid crystal (LC) photo-alignment on the azopolymer films is discussed. As aligning materials we used azopolymalonates and azopolymethacrylates differing by the end substitutes in the azochromophores. The photostimulated self-assembling of azochromophores in the top layer of the aligning film is revealed to be an important factor of LC alignment. It may substantially modify alignment direction and anchoring parameters caused by the photoorientation of azochromophores determined by the light geometry. Depending on the chemical composition of liquid crystal, the self-assembled layers may influence either homeotropic or planar LC alignment. In the latter case azimuthal anchoring is extremely weak so that effective LC gliding can be realized. For the azopolymer with a low self-assembling efficiency tilted LC alignment is realized with the pretilt angle controllable in a range of 0^0-90^0.

1. INTRODUCTION

Nowadays, the photoalignment attracts great attention as one of the most perspective candidate to replace traditional rubbing technique in the new generation of LC displays [1].

The alignment of liquid crystal on the photoirradiated substrate is usually explained by the anisotropic molecular interaction at the LC – substrate interface [1]. The dispersive, polar and steric interactions contribute to this alignment mechanism. In some situations, *e.g.* in case of LC alignment on holographic gratings, the anisotropic surface topology may also be important alignment factor [2].

According to this mechanism, the uniform photoalignment of liquid crystals is a result of uniform alignment of polymer fragments and their photoproducts with an actinic light. The reasons of the molecular ordering under irradiation strongly depend on the prevalent photochemistry of photosensitive fragments. In case of azopolymers, the ordering features are determined by the parameters of *trans-cis* isomerization of azo- fragments. The angular selection or reorientation of *trans* azochromophores perpendicularly to the polarization direction of the actinic light, $\mathbf{E}_a$, may prevail depending on the lifetime of *cis* chromophores [3].

The orientational order of azochromophores determined by the geometry of light irradiation may be substantially modified by the light stimulated processes of self-organization (both bulk and surface processes), especially in the polymer homologues with liquid crystalline properties [4]. In the present paper the light induced self-assembling on the top of the LC aligning films is proved for a large number of azopolymers from the different chemical classes characterized by various temperatures of solidification. A self-assembling of azochromophores, revealing itself in homeotropic LC alignment, is realized by both photoirradiation and heating of the polymer films. In the first case, self-assembling requires a certain irradiation dose and so has a threshold character. It is shown that the self-assembled layers of azochromophores may also induce planar LC alignment with the extremely low azimuthal anchoring energy. This altogether clearly shows important role of self-assembling factor in the liquid crystal photoalignment with polymer films.

2. EXPERIMENTAL

2.1. Aligning materials

We used two series of azopolymers: azopolymalonates differing by the end substitutes in the azochromophores and azopolymethacrylates having different end substitutes and side-chain spacers (Fig.1). The phase transitions in the polymers were studied by polarization microscopy and differential scanning calorimetry. The polymer P1-P3 from the azopolymalonate series show low temperature of solidification, while azopolymethacrylates P4 and P5 keep a glassy state up to 113^0 C and 112 ^{0}C, respectively. The latter polymer also possesses the liquid cryslalline properties in a temperature range of 112^0-140^0 C.

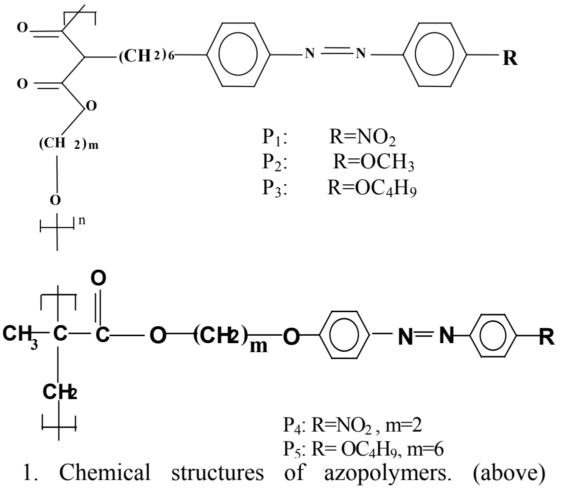

Fig. 1. Chemical structures of azopolymers. (above) – azopolymalonates; (below) - azopolymethacrylates.

2.2. Experimental

The polymer films were prepared by spin coating of polymer solution onto the glass or glass/ITO slides. For this purpose the polymalonates were dissolved in dichloroethane, while methacrylic polymers in dimethylformamide. The weight concentration of polymers in these solutions was about 2 %. The spin velocity was 2500 rpm. The coated films were backed at 90 ^{0}C over 1 h to complete solvent evaporation.

To generate the photoinduced anisotropy, the films were irradiated obliquely with a beam of non-polarized UV light (λ_{ex}=365 nm) from the mercury lamp. The incidence angle of UV light α was varied in order to realize pretilt angle control. The light intensity was about 8 mW/cm^2. Alternatively, the films were two-step irradiated: normally by polarized light (5 mW/cm^2, 10 min) and then, by sample rotation in 90^0, obliquely (α=45^0) with non-polarized light (8 mW/cm^2, 2 min).

The 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 LC cell, the cells were assembled in an antiparallel fashion meaning that the substrates were set so that the vectors specifying the direction of irradiation with non-polarized light were antiparallel to each other. The cell thickness was adjusted by spacers with a diameter of 20 μm. These cells, called with us as symmetrical cells, were used to determine the type of LC alignment, and also to measure pretilt angle and polar anchoring energy. For the azimuthal enegy tests we also constructed cells consisting of rubbed polyimide substrate and photoaligned azopolymer substrate (asymmetrical cells). The easy axis of the azopolymer substrate was turned in 90^0 with respect to the rubbing direction of the polyimide substrate. The cells were filled at room conditions. Systematically we used two kinds of nematic LCs: MLC5700-000 cianobiphenyl mixture with positive dielectric anisotropy and MLC 6610 mixture for VA mode with negative dielectric anisotropy. Additionally we used AM mixture MLC12100-000. The pretilt angle of LC was measured by crystal rotation method [1]. The polar anchoring energy has been measured by the determination of phase retardation for a high voltage applied [1]. The azimuthal anchoring was judged from the twist angle measurement in the asymmetric cells [1].

3. RESULTS AND DISCUSSION

The results of LC alignment are summarized in Table 1.The oblique irradiation with non-polarized light induces homeotropic (LC with $\Delta\varepsilon>0$) or random planar (LC with $\Delta\varepsilon<0$) alignment on the films of polymers P1-P4. This alignment is not influenced by the incidence angle α of UV light.

Table 1. LC alignment on the azopolymer films treated by non-polarized light*.

LC	MLC 5700-000	MLC 6610
P1	h	p(-)
P2	h	p(-)
P3	h	h
P4	h	p(-)
P5	h/tilted	h/tilted

*The letters h and p mean homeotropic and planar alignment, respectively. (-) means certain alignment problems, such as non-uniformity in some cases.

Similar alignment behavior is observed for the films backed above T_c and slowly cooled down to the room temperature. In the latter case, homeotropic alignment is a result of self-assembling of azochromophores at the polymer surface. Naturally that homeotropic alignment in case of photo-excitation is of the same origin.

Interestingly, homeotropic alignment induced by photo-excitation is considerably more stable than that resulted by heating (Fig. 2). This might be cased by total ordering of azochromophores in case of irradiation and only surface ordering due to self-assembling in case of heating. In the latter case, the disordered bulk causes gradual deterioration of surface ordering induced on the stage of heating.

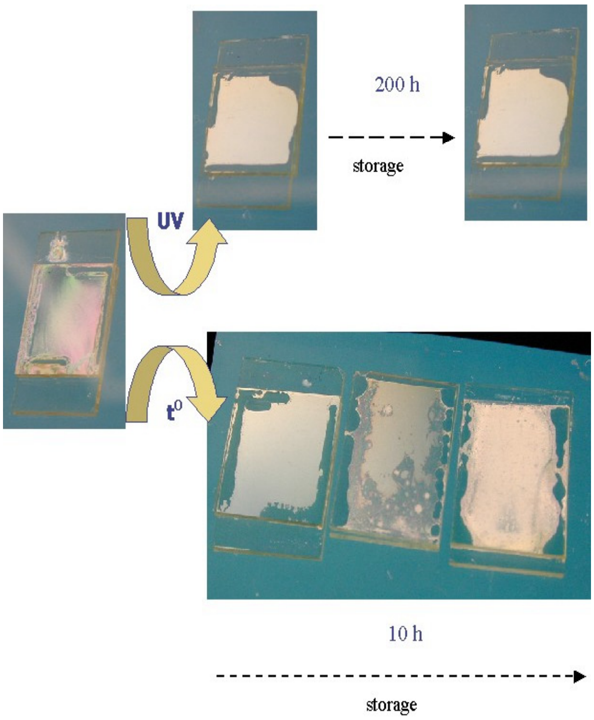

Fig. 2. The scheme demonstrating procedures of homeotropic LC alignment and its aging stability.

The light induced homeotropic alignment has a threshold character: it requires an initiation dosage of about 0.1 J/cm^2. According to Fig. 3 and Fig. 4, it destroys at the high irradiation dose, simultaneously with the aligning film anisotropy. The most probable reason of the alignment deterioration is a destructive photochemistry of azochromophores essential at the high irradiation doses.

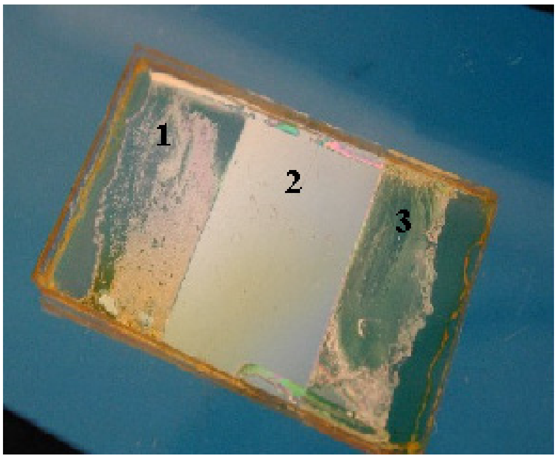

Fig. 3. Photo of symmetric cell filled with LC K15 viewed between two crossed polarizers. The cell contains P3 aligning films. The films are obliquely treated with the non-polarized UV light at the light incidence angle of 45^0. The irradiation time is 0, 15 and 70 min in the cell sections 1, 2 and 3, respectively.

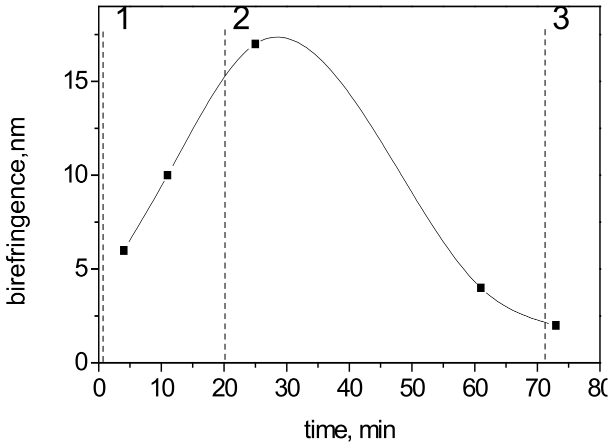

Fig. 4. The photoinduced birefringence in the film of azopolymer P3 vs irradiation time studied by ellipsometry method [4,5]. The numbers 1,2 and 3 mark irradiation doses corresponding to sections 1, 2 and 3 in Fig. 3.

The polymer P5 causes homeotropic or tilted LC alignment depending on either $\alpha=0^0$ or $\alpha\neq0^0$. Figure 5 shows that LC pretilt angle can be wide-range varied with the angle of light incidence. This alignment is characterized by the weak azimuthal and polar anchoring; in case of LC MLC5700-000, the W_a and W_p values are estimated to be $7\ 10^{-7}$ J/m^2 and $8.0\ 10^{-5}$ J/m^2, respectively. Surprisingly, the alignment characteristics on P5 films are similar for both liquid crystals used, *i.e.*, independently on chemical composition of LC.

The difference in LC alignment on P1-P4 and P5 films indicates different surface organization of azochromophores. Homeotropic alignment on P1-P4 films, invariable with the exposure angle, implies effective self-assembling of azochromophores with a spontaneous ordering along the film normal direction. This happens in spite of tilted photo-induced ordering in the polymer bulk governed by the light incidence angle and exposure dose. In turn, controllable pretilt angle on P5 films is an evidence of poor self-assembling so that bulk and surface ordering directions are effectively coupled. This might be caused by the high temperature of solidification (T_g=112 ^{0}C), *i.e.* by the deeply frozen state restricting molecular motions. In addition, comparing with push-pull chromophores (P1 and P4 polymers), a self-assembling in P5 films may be reduced because of two alkyl terminal groups in azochromophores.

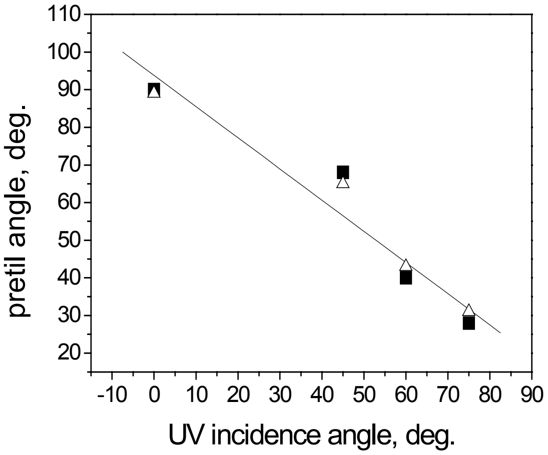

Fig. 5. The LC pretilt angle versus exposure angle plot for the P5 substrate. Squares and triangles represent results for MLC5700-000 and MLC 6610, respectively.

Next point for the discussion is a dependence of LC alignment on the self-assembled layers on the chemical content of LC materials. Due to the dipole- dipole interaction, the dipole moments of azochromophores and LC molecules tend to be parallel. In case of LC molecules, having strong dipole moment along the long molecular axis, the parallel alignment of dipoles should results in a homeotropic LC alignment (Table 1). In contrast, the nematic mixture MLC 6610, having molecules with a transversal dipole moment, should be aligned planar. These expectations fully correspond to our experimental observations. Similar difference in the alignment of LC with positive and negative dielectric anisotropy was observed for SiO$_x$ alignment [6].

Finally, we discuss LC alignment obtained by combination of polarized and non-polarized light. In contrast to only non-polarized irradiation, the homeotropic alignment of cyanobiphenyl based LC is not realized on the P1 films. Instead of it, the combination of polarized and non-polarized light causes nucleation of LC alignment with the high pretilt angle in the alignment domains. This may imply that self-assembled layer on the top of P1 films is damaged. At the same time, the mixture MLC6610 is aligned planarly showing weak azimuthal anchoring. However, W_a is revealed to be extremely weak for the active matrix mixture MLC12100-000, which practically glides on the aligning substrate**.** This makes a couple P1 and MLC12100-000 rather promising for a gliding LCD mode recently suggested [7]. The effective gliding might be caused by the weak dipole-to-dipole interaction at the LC-polymer interface, because of weak molecular polarization of MLC12100-000 molecules that reveals itself in a low dielectric anisotropy.

4. CONCLUSIONS

Thus, the photostimulated self- assembling, in addition to the molecular photoorientation in the aligning film, is an important photoalignment factor.

Usually it leads to homeotropic LC alignment or randomization of the in-plane alignment accompanied with a drastic lowering of azimuthal anchoring energy.

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