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3D Orientational Order in the Photoaligning Polymer Films and its Correlation with LC Alignment

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In this work we study correlation between spatial molecular distributions in the contacting anisotropic polymer films and LC layers. Two kinds of side-chain azopolymers were employed: with the azochromophores containing hydrophobic OC_4H_9 alkyl chain (P1) and strongly polar NO_2 group (P2) as the end substituences, respectively. The tilt orientation of azochromophores was induced by the oblique irradiation of the polymer films with non-polarized UV light. The tilt angle was controlled by the change of the angle of the UV light incidence. The uniform alignment of several LC with the quasilinear dependence of the LC pretilt angle on the inclination angle of azochromophores was observed for the films of P1. In contrast, the alignment of LCs on the films of P2 strongly depended on the structure of LC molecules and did not depend on the inclination of azochromophores in the polymer bulk. Possible reasons of the difference in results obtained for P1 and P2 are discussed.

Kyewords: azopolymer; photoinduced anisotropy; photoalignment; liquid crystal; pretilt angle.

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1. INTRODUCTION

The phenomenon of photoinduced anisotropy in polymer films is of great interest for the modern LCD technologies. This is caused by possible application of this effect for manufacturing LCD elements (retardation films, polarizers *etc.*) [1,2] and for liquid crystal (LC) alignment [3, 4]. The LC photoalignment method is free from the principle drawbacks of the traditional rubbing procedure and so it may replace rubbing in the in the new generation of LCD. However, several technological problems should be solved associated with thermal stability of the induced alignment, pretilt angle control, and image sticking [5]. These problems are under intensive study now.

In the present work we consider principle difference between LC photoalignmnet and rubbing technique. The rubbing method modifies mainly surface of the aligning polymer substrate. At the same time, the actinic irradiation penetrates through the polymer film modifying both polymer surface and bulk. We believe that spatial molecular orientation in polymer bulk influences surface molecular distribution and surface relief, which, in turn, determine the 3D director configuration of LC layer. The bilayer “aligning polymer-LC” can be considered as a contact of two interacting orientationally ordered phases. The influence of these phases each on other is not equal. The polymer film influences alignment of all LC layer due to the high correlation length of LC. In contrast, LC may only influence the structure and properties of “LC-polymer” interface [6]. In other words, LC may, in a certain degree, mimic the orientational structure of the photoordered polymer film. The correlation between spatial molecular orientation in polymer film and director configuration in LC layer is a general question of our studies. In the present work we try to find correlation between inclination of the molecular fragments in the polymer films and LC pretilt angle.

2. EXPERIMENTAL

2.1. Samples

We used two azopolymers to prepare photoaligning layers. The polymer 1 (P1) was LC polymethacrylate containing 4-hexoxy-4'-pentoxyazobenzene fragments as the side chains. Synthesis and characterization of this polymer is described in [7]. It forms nematic mesophase in the interval 112-140 °C. The polymer 2 (P2) was LC polyester containing 4-nitro-4'-hexoxyazobenzene side-chain groups. Synthesis of P2 was described earlier in [8]. The polymer P2 forms smectic A and nematic mesophase in the temperature intervals 44-52 °C

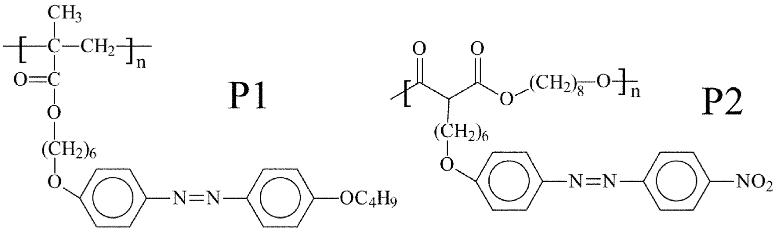

FIGURE 1 Structural formulae of the studied polymers.

and 52-55 °C, respectively. Structural formulas of P1 and P2 are presented in Fig.1.

The polymer films were obtained by spin coating of the polymer solution in diclorethane (at the polymer concentration of 10 g/L) on the glass slabs. A thickness of the films was about 500 nm. The films were kept at the elevated temperature (T=50 °C) over 3 h and subsequently irradiated by polychromatic irradiation of the Xe lamp. The actinic light was non-polarized, collimated, and directed obliquely to the film plane. The irradiation intensity and irradiation time were 12 mW/cm^2 and 10 min, respectively. The incidence angle of the light was varied within 0° and 80°.

The irradiation with non-polarized light was employed to induced simple 3D orientational structures (uniaxial structures) in azopolymer films, which can be easily compared with the spatial director field in LC layers.

To prepare cell the substrates were combined in the way providing antiparallel LC alignment. The cell gap was maintained with the spacer bolls of 20 μm in diameter. The cells were filled at the room temperature with nematic LC 5CB, E7 and ZLI 4801 purchased from Merck.

2.2. Methods

The spatial distribution in azopolymer films was studied by the null ellipsometry technique. This method is modified Senarmont method [9] extended for the oblique incidence of the testing light to estimate both in-plane and out-of-plane (with respect to the film plane) birefringence of the anisotropic samples. The analyzer rotation angle versus sample rotation angle curves were measured experimentally as well as calculated theoretically for various orientational structures of the tested films. The experimental curves were fitted with the theoretical one calculated in frame of the most suitable orientational model. The measurements were carried out 10 min after each irradiation step in order to reach stationary state. The fitting gives both in plane n_y-n_x and out-of-plane n_z-n_x birefringence values (x, y, z are principle axis of the film (Fig.2)). The n_y-n_x and n_z-n_x coefficients were estimated for various irradiation doses. The direction of the preferential orientation of azochromophores is determined as the direction of maximal refractive index of the film. The details of the method were recently published in [10].

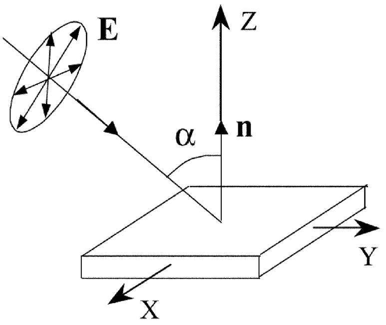

FIGURE 2 Irradiation geometry and principle axes of polymer probe.

The preliminarily investigated azopolymer films were employed to produce LC cells. The quality of LC alignment was controlled by observation of the samples by naked eyes through the crossed polarizers as well as in the polarizing microscope. The pretilt angle in LC cells was measured by crystal rotation method [11]. The accuracy of the pretilt angle measurements was about 0.3°.

3. RESULTS

The orientational distributions of azochromophores in the spin coated films of both polymers are spatially anisotropic; the chromophores in the P1 film are preferentially aligned in plane of the film, whereas in the P2 samples in the direction of the film normal. In other words, films of P1 and P2 posses positive and negative uniaxial order, respectively. The ordering axis in both cases coincides with the film normal.

The orientational order in azopolymer films was generated by the oblique irradiation with collimated non-polarized light as described in paragraph 2.2. The orientational structures of azochromophores induced in P1 for each irradiation dose were fitted well in frame of the uniaxial model with an ordering axis tilted in the direction of the light incidence. The phase retardation $(n^e-n^o)d$ and the tilt angle of the ordering axis θ_a (the angle between the film plane and the ordering axis) depended on the irradiation time with a saturation at high irradiation doses. The obtained results are presented in Fig.3.

The orientational structures induced in P2 were more complicated. In general case, these structures are biaxial and can be considered as a composition of two uniaxial sub-structures undergoing one into other with the increasing of the irradiation dose. The first sub-structure is of the same type as the structure of the non-irradiated film. The axis of the second sub-structure lies in the plane of the light incidence and forms angle θ_a with the film plane. The contribution of the sub-structure 2 increases with the increase of irradiation dose. Finally, in the photosaturated state, the only sub-structure 2 is realized and so tilted uniaxial orientation of azochromophores is reached.

Thus, in spite of the difference in the first period of structural changes, the structures realized in the saturated state of irradiation are quite similar in both polymers. They are characterized by oblique uniaxial orientation of azochromophores. In the following, the irradiation time corresponded to the saturation part of the structural changes, i.e. to the induction of uniaxial orientation. The structures induced in the

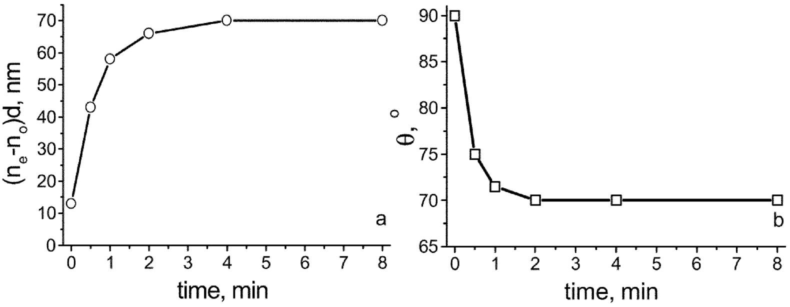

FIGURE 3 The n^e-n^o (a) and θ_a (b) estimated for P1 film as the functions of irradiation time. The probe is irradiated with non polarized light with the incidence angle α=45°.

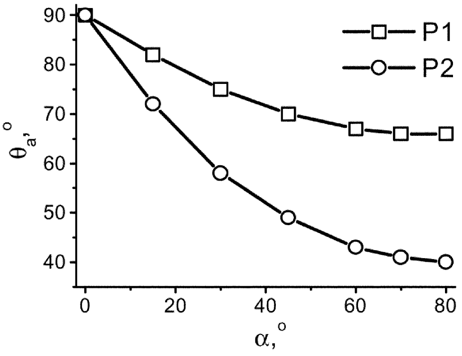

FIGURE 4 The θ_a versus α curves for P1 (1) and P2 (2) films. The values of θ_a corresponds to photosaturation part of $\theta_a(t)$ curves (see Fig.3).

saturated state were estimated for different incidence angles of the exciting light. The tilt angle of such structures, θ_a, is revealed to be a function of the light incidence angle α. The θ_a vs α curves measured for both P1 and P2 films are presented in Fig.4.

On the next stage, the polymer films with estimated orientational structure were used as aligning substrates for LCs. The non-irradiated films of P1 provided homeotropic alignment of LCs used in our studies. In contrast, planar LC alignment with the degenerated alignment direction in the film plane was detected for the non-irradiated films of P2. The films of P1 irradiated with non-polarized light provided uniform alignment of LCs with the variable pretilt angle. The dependencies of the LC pretilt angle, θ_{LC}, on the tilt angle of azochromophores in P1 film, θ_a,

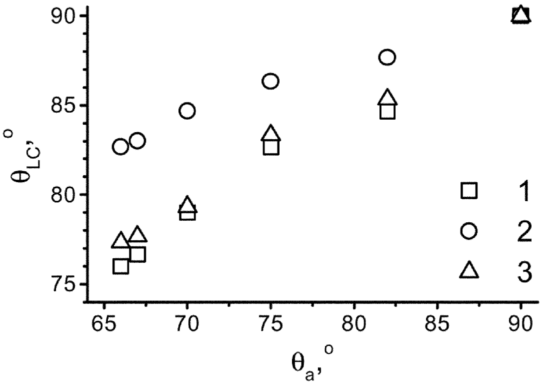

FIGURE 5 The θ_{LC} versus θ_a curves for the cells based on P1 substrates irradiated with non-polarized light at different incidence angles. Different curves corresponds to the cells filled with different LC: 1- 5CB; 2- E7; 3- ZLI-4801.

obtained for various LCs are presented in Fig. 5. The θ_{LC} vs θ_a curves are linear with good approximation. It shows strong correlation between ordering direction of azochromophores and LC pretilt.

Qualitatively other results were obtained for the P2 films. No uniform alignment of LC ZLI 4801 was detected for the films irradiated obliquely with the non-polarized light. At the same time, LCs 5CB and E7 were aligned homeotropically independently on the light incidence angle.

4. DISCUSSION

In spite of quite similar photoinduced orientation of azochromophores in the polymer bulk, the P1 and P2 films exhibit strongly different LC aligning properties. Several reasons can be responsible for this difference depending on the dominant mechanism of "LC-polymer" interaction. Let us at first assume that LC alignment is mainly determined by the steric interaction of LC with azochromophores on the polymer surface. This factor may be especially strong when "LC-polymer" interface is diffuse. It means that LC molecules at interface are incorporated in the surface polymer layer and so they are completely influenced by the order of surface azochromophores. In this case the difference in the orientational order of LC and azopolymer layer should be mainly determined by the difference in ordering of the bulk and surface azochromophores.

In contrast to the first case, let us suppose that steric factor is a secondary one, whereas the main role play other components of "LC-polymer" interaction (electrostatic, dispersion *etc.*), which are strongly dependent on the chemical structure of both compounds. This factor may be decisive one when the boundary between LC and polymer is more or less clear, i.e. when LC molecules do not penetrate in the polymer layer. In this case LC forms boundary layer over the surface layer of polymer. The structure of this layer should be determined by the molecular interaction “LC-polymer” and “LC-LC”.

In the following we will consider results related to LC alignment taking into account the points discussed above. Let us first try to find explanation assuming steric factor as a decisive one for LC orientation. With this we assume that the surface of polymer films is fairly crumbly so that LC molecules penetrate into the polymer. This is more probable for the polymer P1 containing hydrophobic tails. One can speculate that due to these tails azochromophores are oriented preferentially normally to the film surface similarly to the homeotropic ordering of the surfactant materials. In contrast, the azochromophores on the P2 surface are presumably in-plane oriented. The possible reason of the in-plane alignment may be dipole-dipole interaction of the strongly polar azochromophores with the polar groups from the polymer backbones forming polymer surface (see Fig.1). These assumptions may explain why LCs are aligned homeotropically on the P1 films and planarly on the P2 films.

To explain the correlation between LC pretilt and inclination of azochromophores in P1 film, we should assume that orientational order of the surface part of azochromophores is fairly similar to the bulk one. It means that oblique irradiation with non-polarized light causes inclination of azochromophores in the bulk of P1 films and on the surface as well. In turn, the tilted surface azochromophores cause LC pretilt.

In big contrast to P1 polymer, it is difficult to explain aligning properties of the irradiated P2 films taking into account only steric factor. Indeed, it is hard to understand why ZLI 4801 does not align uniformly on such films, while 5CB and E7 align homeotropically. It is also unclear why the LC alignment does not depend on the light incidence angle. To explain these results we should assume that the non-steric components of the "LC-azochromophore" interaction play important role in LC alignment. As it was mentioned above, the role of these types of interaction can be decisive one at the fairly clear LC-polymer interface, when self-assembling of the LC layer at a polymer surface can be realized. Unfortunately, we do not have now direct experimental proofs of that it is the case for P2. However, some results obtained additionally for P2 are in good agreement with this suggestion.

Taking into account photoorientation factor one should assume that azochromophores reorient in the direction of light propagation in both polymer bulk and on the polymer surface. In case of P2 the reorientation out of the film plane should be realized. Note, that for the polymer bulk this is confirmed by the ellipsommetric studies. In addition to the photoorientation, the out-of-plane ordering on the surface of P2 film can be influenced by the one more important factor. As it was mentioned before, the P2 polymer is characterized by low temperatures of mesophases (44-55 °C). The actinic light irradiation may substantially reduce transition temperatures of the polymer due to the both direct heating and generation of *cis*-isomers [12]. The photoinduced melting and transition to the mesophase was directly observed in P2 films at the irradiation conditions used in our experiments. Hence, the processes of self-organization characteristic for mesophases may play important role in the formation of orientational order [13,14]. One can suppose, that mesogenic azochromophores orient normally to the "film-air" interface similarly to the low-molecular-weight LCs [15-17]. The surface concentration of azochromophores may be enhanced by the light stimulated diffusion from the polymer bulk. As result of these processes, polar ordering of the chromophores should be realized at the polymer surface. The assembling of the surface chromophores containing strong dipole groups NO_2 can be reached at the effective interaction of its aromatic cores. The possible mechanism is $\pi\pi$-interaction with the formation of H aggregates as it takes a place in the bulk of this polymer [14]. Such kind of interaction suggests compact packing of azochromophores. Hence, the efficiency of the penetration of LC in the polymer should be low and so the role of steric component of "LC-polymer" interaction should be diminished. The out-of-plane reorientation of the surface azochromophores containing strongly polar NO_2 tail groups should cause essential increase of the polarization of polymer surface. This may explain homeotropic alignment of LCs containing polar heads (interacting with polar surface) and hydrophobic tails (trying to be oriented normally to the film). The examples of such LCs are 5CB and E7. In contrast, LCs containing hydrophobic tails from the both sides of the molecular core should poorly interact with the polar surface. It may explain poor alignment of LC ZLI 4801 on the P2 films irradiated with non-polarized light.

Since alignment of 5CB and E7 on the irradiated substrates is homeotropic and it does not depend on the angle of light incidence, we can not answer the question whether the azochromophores are homeotropically or obliquely aligned at the surface of P2. The explanation of the homeotropic alignment of 5CB and E7 presented above is valid for both normal and oblique orientation of azochromophores, since in both cases the surface polarization and the chromophore packing may be high.

Thus, non-steric factors of “LC-polymer” interaction can strongly influence LC alignment especially in the polymers containing polar azochromophores. However, even for the azochromophores with low polarity the role of this factor is essential. Particularly, it may explain various inclination of the θ_{LC} vs θ_a curves obtained for various LCs aligned on P1 films (see Fig.5).

Of course, the model suggested to explain experimental results contains several assumptions which should be additionally proven. First of all the modification of the polymer surface with the UV light should be deeply studied. Some new results related to this problem will be published in our forthcoming paper.

5. CONCLUSIONS

The bilayer „anisotropic azopolymer-LC“ is considered as a binary system of the mutually influenced anisotropic phases possessing „frozen“ and spontaneous orientational order, respectively. The linear dependence between the LC pretilt and the tilt of azochromophores in the aligning azopolymer film is observed. This shows that spatial orientation of LC may strongly correlate with the spatial distribution of azochromophores in the aligning films. This correlation is assumed to be especially strong for the bilayers “polymer-LC” characterized by a broad interface with the mutually penetrated LC and polymer components. In this case the LC effectively mimic the orientational structure of the polymer film. In contrast, the difference in bulk and surface orientation of polymer films (for instance, caused by strong aggregation of azochromophores on the polymer surface or polar orientational order) and effective "LC-polymer" interaction may destroy orientational correlation between polymer film and LC layer. To study the problem deeply, the order transfer in the sequence "polymer bulk-polymer surface-LC" should be comprehensively investigated.

Acknowledgments

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