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Three-dimensional orientational order in the bulk and on the surface of polymer films and its effect on liquid-crystal alignment

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The correlation between orientation ordering of polymer chains in the bulk of polymer film and at the polymer–liquid-crystal (LC) interface has been studied to determine its role in LC alignment. The bulk and surface ordering of polymer were investigated by null ellipsometry and x-ray reflectivity, respectively. Two kinds of liquid-crystalline polymers were used; side-chain azopolymers with azochromophores containing hydrophobic OC₄H₉ alkyl chain (*P1*) and strongly polar NO₂ group (*P2*) as the end substituents. The uniaxial tilt orientation of azochromophores in the films of both polymers was induced by the oblique irradiation with unpolarized UV light. The two polymers exhibit similar chain orientation but different ordering of azochromophores on the surface of the films of *P1* and *P2*. Surface ordering of *P1* films correlates very well with the order in the bulk of the film, which are essentially determined by the UV exposure. However, orientational order of polymer chains at the surface of *P2* films is different from that in its bulk and is not determined by UV exposure. This is explained by strong aggregation of azochromophores during its self-assembling at the polymer-air interface. The LC alignment is determined by the surface ordering of azochromophores. The results imply that ordering tendency can be effectively transferred from polymer bulk to polymer surface and then to LC if it is not lost at the polymer-LC interface.

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I. INTRODUCTION

Polymers which can be orientationally ordered under UV irradiation have numerous potential applications in photonic devices, data storage, optical information processing and communications, and integrated optics [1]. Furthermore, anisotropic polymer films are of great utility in modern liquid-crystal display (LCD) technologies because of their use in manufacturing LCD components such as alignment layers [2,3], retardation films, and polarizers, etc. [4,5]. Since LC photoalignment method is free from the drawbacks of the traditional method of *rubbing*, it is preferable for next generations of LCDs. However, there are several technical issues associated with photoalignment that need to be addressed, such as thermal and photostability of alignment, pretilt angle control, and image sticking [6].

The rubbing method mainly modifies the surface of the polymer film. On the other hand, UV radiation penetrates the polymer film modifying both its surface and the bulk structures. The polymer-LC interface can be considered as the plane of interaction between the LC on one side and polymer bulk on the other. Both the bulk polymer and the LC can, in principle, determine the structure and properties of the LC-polymer interface [7,8]. However, the interface structure cannot influence the structure of solid polymer film characterized by “frozen” orientational order. In contrast, alignment of LC layer is easily governed by boundary conditions because of the long-range orientational interaction between the two. In other words, LC alignment mimics, to a certain degree, the orientational order of the polymer film caused by

UV exposure. How exactly this takes place is not only of scientific interest but also very useful to better understand the mechanism responsible for the pretilt, and account for the anchoring energy and image sticking. Answer to these questions should help in solving problems, which hamper implementation of the photoalignment method in commercial applications.

We report here the results of our comprehensive attempt to seek answer to the above questions. The orientational order in the bulk and on the surface of polymer films, as well as LC alignment are studied by several independent methods. The results show that correlation between orientations of polymer and LC layers strongly depends on the physical structure of the interface which is determined by the chemical structure of polymer and LC molecules. A simple model of the interface ordering is discussed to explain the results.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Two azopolymers were used to prepare the photoalignment layers. One of the polymers *P1* was a polymethacrylate containing 4-hexyloxy-4'-pentoxyazobenzene LC fragments as side chains. The polymer *P2* was LC polyester containing 4-nitro-4'-hexyloxyazobenzene side-chain groups. Structural formulas of the polymers are presented in Fig. 1. The synthesis procedures of *P1* and *P2* were previously described in Refs. [9,10]. Phase transitions in the polymers were studied by differential scanning calorimetry and polarization microscopy methods. *P1* is characterized by relatively high glass

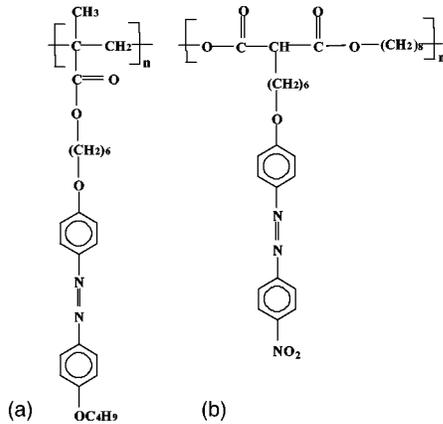


FIG. 1. Structural formulas of (a) polymer *P1* and (b) polymer *P2*.

transition temperature of $\sim 112^\circ\text{C}$. In contrast *P2* possesses a partially crystalline state at room temperature which melts at 44°C . Both polymers have LC properties above the glass/melting points. *P1* exhibits a nematic phase between 112°C and 140°C . Polymer *P2* forms the smectic and the nematic mesophase between 44°C and 52°C and 52°C and 55°C , respectively.

The polymer films were deposited by spin coating of polymer solutions in dichloroethane on to precleaned glass slides purchased from Fisher Scientific. The thickness of the films was varied between 50–200 nm by changing spinning speed and polymer concentration of solutions. Their thickness was measured by a profilometer.

The deposited films were kept at an elevated temperature (40°C) for over 6 h and subsequently irradiated by polychromatic UV radiation from a Xe lamp (Oriol Corp.). The actinic or UV light was unpolarized, collimated, and made incident obliquely on to the film. The intensity and exposure time were 12 mW/cm^2 and 10 min, respectively. The angle of incidence of light α_{UV} was varied between 20° and 90° . The projection of the wave vector of UV light defines the x axis in the plane of the film (Fig. 2).

To prepare LC cells, two substrates were assembled to provide antiparallel LC alignment. The cell gap was maintained with spacer strips of $20\ \mu\text{m}$. The cells were filled at the room temperature with nematic LC 5CB, E7, and ZLI 14801 from Merck.

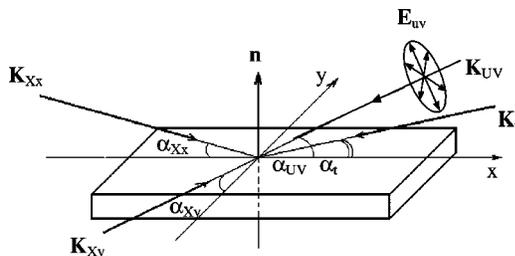


FIG. 2. Sample orientation with respect to the UV beam with wave vector \mathbf{K}_{UV} , probe beam with wave vector \mathbf{K}_t , and incident x-ray beam with wave vector \mathbf{K}_{xi} ($i=x,y$). n is surface normal. x and y axes lie in substrates plane.

B. Experimental methods

Spatial orientation of azochromophores in the polymer films was studied by the null ellipsometry (NE) technique. This method is a modified Senarmont method [11] extended for oblique incidence of the probe light to estimate, both, in-plane and out-of-plane birefringence. The probe beam's ($\lambda_t=0.63\ \mu\text{m}$) angle of incidence α_t was varied by sample rotation about the surface normal. The analyzer angle φ vs sample rotation angle α_t curves were measured for two orientations of the test samples with sample (x -) axis oriented horizontally and vertically. Dependence of φ on α_t was calculated using Berreman's 4×4 matrix method for various types of birefringent layers including uniaxial and biaxial layers with various orientation of the optic axis. The experimental data were fitted to theoretical functions corresponding to the most suitable orientation model. The fits gave, both, the in-plane (n_y-n_x) d and the out-of-plane (n_z-n_x) d phase retardations (x, y, z are principle axes of the film). The birefringence coefficients n_y-n_x and n_z-n_x can be estimated if the film thickness d is independently known. Moreover, the fits allow one to estimate spatial orientation of optic axes of the anisotropic films. The direction of the preferential orientation of azochromophores was determined from the direction of the maximum value of the measured refractive index. Consequently, information about the orientation of azochromophores was deduced from the orientation of the axes of the index ellipsoid of the film.

Films were irradiated in discrete steps. After each irradiation, the measurements with null ellipsometry technique were performed. A 15 min pause between irradiation and measurements was used to ensure a steady state. The details of the NE method as well as its application to azopolymers can be found in our recent publications [12,13].

The x-ray reflectivity (XRR) measurements were used to determine molecular orientation at the polymer film's surface. In the case of the cast polymer film, the x-ray reflectance is determined by air-film and film-glass interfaces. The interference of waves reflected from these two interfaces results in Kiessig fringes, containing information about the film thickness, electron density gradients in the direction perpendicular to the substrate, and vertical rms roughness σ of the interfaces. In addition to the effect of surface topology on the alignment of LC, the surface roughness was used to estimate surface packing at the polymer surface. In this case, we assumed that tight molecular packing results in a smoother polymer film.

The roughness of the polymer films, before and after UV irradiation, was determined by specular XRR measurements using $\text{Cu } K\alpha$ radiation from an 18 kW Rigaku rotating anode generator and a four circle Huber goniometer. A pair of polished Si (111) crystals were used as a monochromator and analyzer to achieve high resolution, $|\Delta\mathbf{q}|\sim 10^{-4}\ \text{\AA}^{-1}$. Two specular longitudinal scans (i.e., scattering vector in the direction perpendicular to the film) were carried out in two different azimuthal orientations of the sample. For one scan, the scattering plane of x rays contains the direction (x direction in Fig. 2) of incidence of UV light. For the second scan, the sample was rotated by 90° about the surface normal so

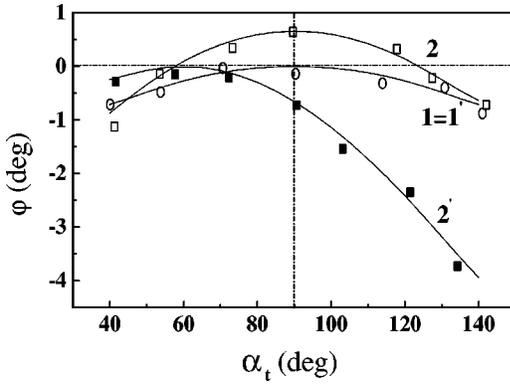


FIG. 3. Analyzer angle vs sample rotation curves for films of polymer *P1* before (curves 1, 1') and after (curves 2, 2') UV irradiation ($\alpha_{uv}=45^\circ$, $I=12$ mW/cm 2 , and $t=10$ min). Curves 1, 2 and 1', 2' correspond to vertical and horizontal orientations, respectively. According to the model used, $n_x=n_y=n^o < n_z=n^e$, $(n^e-n^o)d=5$ nm, $\theta_a=90^\circ$ (before irradiation) and $(n^e-n^o)d=30$ nm, $\theta_a=71^\circ$ (after irradiation).

that the x direction was perpendicular to the scattering plane (Fig. 2). Additional description of the experimental set up, procedure, and data analysis can be found in Refs. [14,15].

The quality of LC alignment was judged by visual inspection of the samples placed between crossed polarizers as well as under polarizing microscope. The pretilt angle in LC cells was measured by the crystal rotation method [16]. The accuracy of the measured pretilt angles was about $\pm 0.3^\circ$.

III. RESULTS

A. Alignment of azochromophores in the polymer bulk

The φ vs α_t curves obtained for the nonirradiated films of *P1* are marked as 1 and 1' in Fig. 3. The curves obtained for horizontal and vertical orientation of the x axis are essentially identical and show isotropic distribution of azochromophores in the film plane. The fitting procedure gives $n_x=n_y=n^o < n_z=n^e$ establishing uniaxial ordering of azochromophores in the normal direction. At the same time, low phase retardation, i.e., $(n^e-n^o)d=5$ nm and $(n^e-n^o)=0.02$, implies poor ordering of azochromophores. The results obtained for *P2* film were quite similar to those for *P1* except for somewhat smaller value of n^e-n^o [17].

The typical φ vs α_t curves for the obliquely irradiated *P1* film are marked as 2 and 2' in Fig. 3 for vertical and horizontal orientation of the x axis, respectively. These data fit well to the uniaxial model with the ordering axis tilted in the direction of the incidence of light. The birefringence n^e-n^o and the tilt angle of the ordering axis θ_a with respect to the film's plane change with the exposure time showing a saturation at high irradiation doses (Fig. 4). Qualitatively similar behavior is observed for *P2* films.

In subsequent measurements, we avoided transient effects by using long irradiation time to take the system to saturation. The structures induced in the saturated state were estimated for different angles of incidence of the UV light. The tilt angle of such structures, θ_a (the angle between ordering axis of azochromophores and film plane) is found to depend

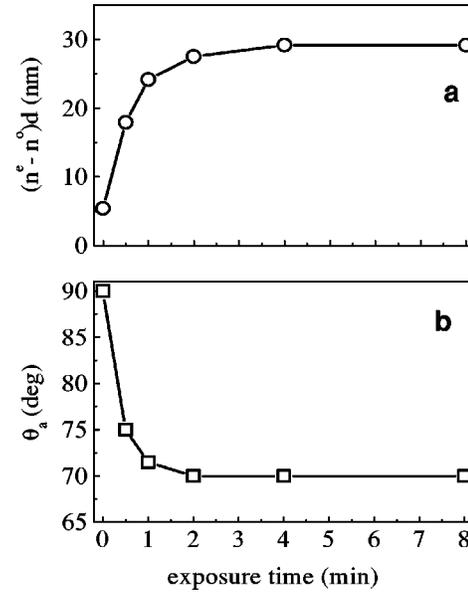


FIG. 4. Phase retardation (a) and tilt angle of azochromophores (b) in *P1* film, as functions of irradiation time. Irradiation is performed at $\alpha_{uv}=45^\circ$, $I=12$ mW/cm 2 .

on the incidence angle α_{uv} . The θ_a vs α_{uv} curves obtained for *P1* and *P2* are presented in Fig. 5(a) and Fig. 6(a), respectively. The correspondence between the values of the tilt angle of azochromophores and the angle of incidence of UV light shows that the azochromophore bulk orientation is effectively governed by UV light.

B. Surface structure of the azopolymer films

In the case of polymer films deposited on glass substrates, the x -ray reflectivity is determined by the roughness of both glass-polymer and polymer-air interfaces. In order to estimate polymer-air roughness, the roughness of bare glass plates was measured *a priori*. The reflectivity scans were performed in the (x,z) and (y,z) planes. Fits to these scans revealed isotropic surface morphology of the films with rms roughness $\sim 3.0 \pm 0.5$ Å.

Frequently, the reflectivity scans of the polymer films measured in (x,z) and (y,z) planes were slightly different revealing slight anisotropy of surface roughnesses caused by the spin coating process during film preparation. To avoid the influence of the initial anisotropy, the films with practically isotropic surface were selected for further studies. The (x,z) and (y,z) scans for the nonirradiated film of *P1* are shown in Fig. 7. The fits yield vertical rms roughnesses in x and y directions to be 19 ± 1 Å. Using the formula $d = m\lambda/2(\sin \alpha_{x1} - \sin \alpha_{x2})$, where m is number of fringes and α_x is x -rays' incidence angle (Fig. 2), the thickness d of azopolymer *P1* film was determined to be ~ 330 Å.

Figure 7 also shows the reflectivity scans for the *P1* film irradiated at an incidence angle $\alpha_{uv}=90^\circ$. The estimated value of the roughness is 24 ± 1 Å in both x and y directions. Values of the surface roughness σ were obtained for various

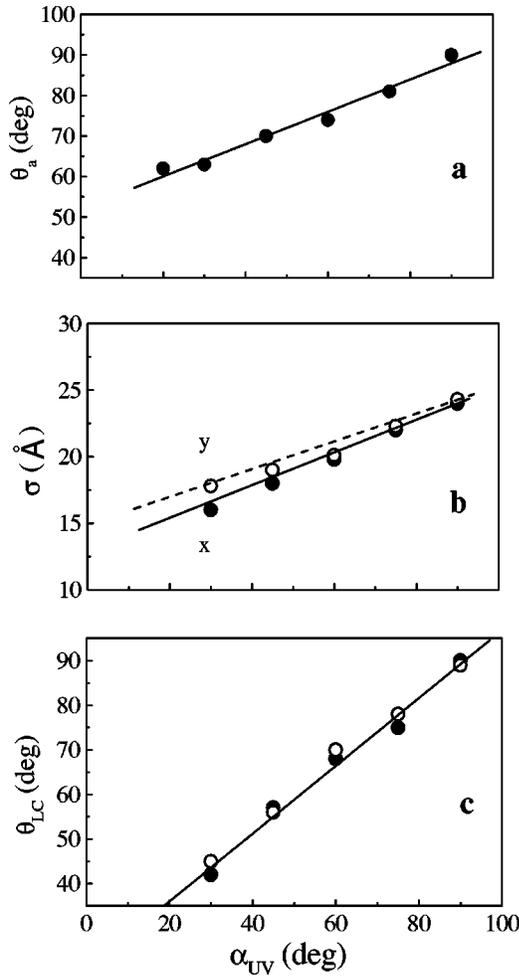


FIG. 5. Azochromophore tilt angle (a), surface roughness (b), and LC pretilt angle (c) as functions of the angle of incidence of UV light for P1 films. The irradiation parameters are $I=12 \text{ mW/cm}^2$, $t=10 \text{ min}$. In (b) data marked with x and y correspond to roughness in the x and y directions of the film. In (c) solid and open circles correspond to LC 5CB and LC ZL14801, respectively.

angles of incidence of UV light. The samples used for irradiation at various angles were of the same thickness to within $\pm 15\%$. The measurements were carried out within 6 h after irradiation. The plots of rms roughness in x and y directions vs incidence angle of light are shown in Fig. 5(b). As can be seen, the roughness of the irradiated films increases quasilinearly with the UV's incidence angle, and is maximal for normal irradiation. For normal incidence, the film's roughness is 1.35 times higher than that of nonirradiated films. At the smallest incidence angle of UV light used in these experiments ($\alpha_{UV}=30^\circ$), the anisotropy in the surface roughness was found to be $3 \pm 1 \text{ \AA}$. This means that the film is slightly rougher in the y direction, i.e., in the direction perpendicular to the plane of the UV light's incidence.

Specular scans for the P2 films are presented in Fig. 8. Thickness of these films is estimated to be $\sim 1000 \pm 100 \text{ \AA}$. The distinctive feature of P2 films is a sharp increase in the amplitude of Kiessig fringes after irradiation. This implies a considerable smoothing of the film's surface. Roughness of

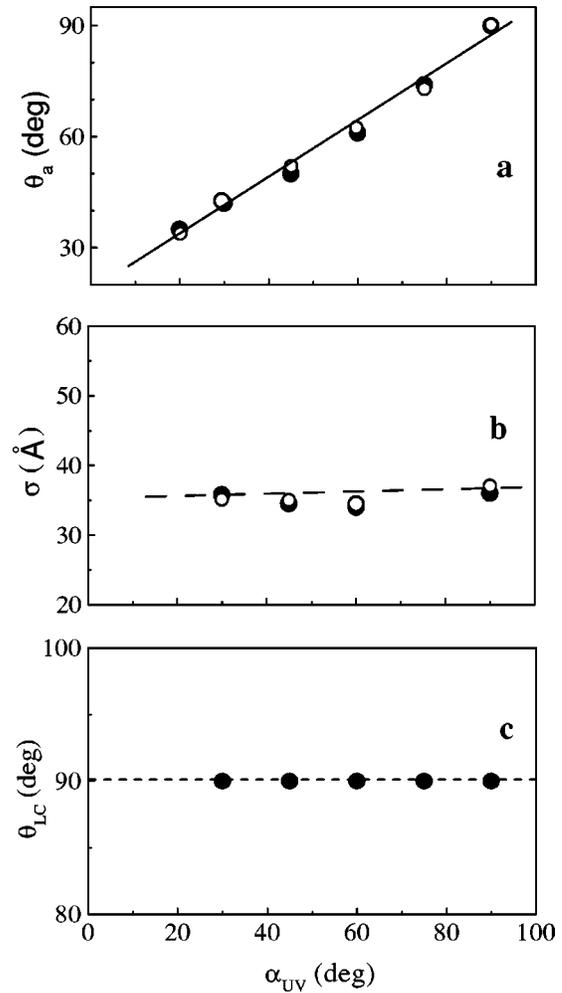


FIG. 6. (a) Azochromophore tilt angle, (b) surface roughness in the x and y directions of the film, and (c) LC pretilt angle for LC 5CB and E7 as functions of the angle of incidence of UV light. The irradiation parameters are $I=12 \text{ mW/cm}^2$ and $t=10 \text{ min}$.

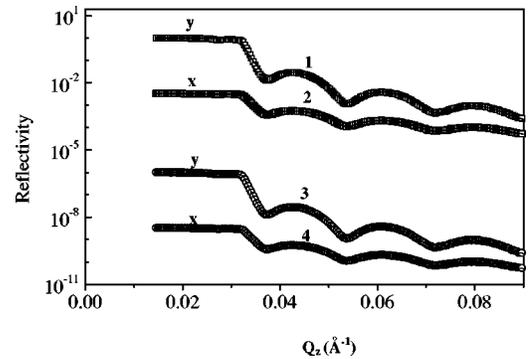


FIG. 7. Specular reflectivity scans for a film of P1, before and after irradiation with nonpolarized UV light ($\alpha_{UV}=90^\circ$, $I=12 \text{ mW/cm}^2$ and $t=10 \text{ min}$). The scans are presented for x and y orientations of the sample. Fits yield $\sigma=19 \pm 1 \text{ \AA}$ (nonirradiated film) and $\sigma=24 \pm 1 \text{ \AA}$ (irradiated film).

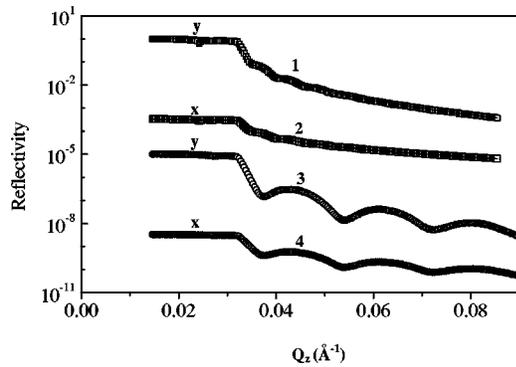


FIG. 8. Specular reflectivity scans for the film of polymer $P2$ before and after irradiation with nonpolarized UV light ($\alpha_{uv} = 90^\circ$, $I = 12 \text{ mW/cm}^2$ and $t = 10 \text{ min}$). The scans are presented for x and y orientations of the sample. Fits give $\sigma = 55 \pm 1 \text{ \AA}$ (nonirradiated film), $\sigma = 36 \pm 1 \text{ \AA}$ (irradiated film).

the irradiated film is $\sim 33\text{--}36 \text{ \AA}$ in contrast to 56 \AA before irradiation. Plots of the rms roughness vs the angle of UV's incidence for $P2$ films are presented in Fig. 6(b). They show that the roughness essentially depends on the inclination of azochromophores in the bulk determined by the angle of light incidence. Furthermore, the anisotropy in the surface roughness is negligibly small.

C. LC alignment

In the next phase of our studies, polymer films with the uniaxially inclined chromophores were used as aligning substrates for LC. The nonirradiated films of $P1$ provide homeotropic alignment for all LCs used in our studies. In contrast, the nonirradiated films of $P2$ do not align the LC uniformly.

The films of $P1$ irradiated with nonpolarized light provide uniform alignment of LC with a variable pretilt angle. The direction of LC pretilt is the same as the tilt direction of azochromophores and corresponds to angle of incidence of the UV light. Data showing the dependences of the LC pretilt angle θ_{LC} on the tilt angle of azochromophores in polymer films θ_a obtained for various LCs are presented in Fig. 5(c). The θ_{LC} vs θ_a curves are linear to a good approximation. This establishes good correlation between the axis of LC alignment and direction of the ordering of azochromophores.

Qualitatively, a very different result is obtained for $P2$ films obliquely irradiated with UV. No uniform alignment of

LC ZLI 4801 was detected. At the same time, LC 5CB and E7 aligned homeotropically independently of the direction of UV's incidence [Fig. 6(c)].

IV. DISCUSSION

Let us now come back to the main question, i.e., to what extent does the LC layer mimic orientational structure of photoaligning layer? As noted above, in the case of $P1$ films, LC alignment correlates very well with the bulk alignment of azochromophores. But such a correlation is not observed in the case of $P2$ films. The reason for this difference seems to be different ordering of azochromophores at the surface of polymer film, which determines the surface morphology and LC-polymer interaction. In case of $P1$, these results confirm roughening of the films caused by normal irradiation and quasilinear increase of the vertical rms roughness with increase in the angle of UV's incidence. These results may be explained by assuming that the roughness is determined by the alignment of azochromophores at the polymer's surface. Figure 9 illustrates how the polymer surface may become smoother via tilting of azochromophores upon oblique exposure to UV. Similarly, normal irradiation causes reorientation of azochromophores nearly perpendicularly to the surface resulting in an increase of surface roughness. Thus, studies of surface roughness indirectly confirm that surface alignment of azochromophores in $P1$ film is governed by UV light. Taking into account that the same tendency holds true for the bulk, one can conclude that the orientation of azochromophores in the bulk and at the surface are clearly and strongly correlated.

In $P2$ films, normally incident radiation causes a strong decrease in the value of surface roughness. Noteworthy is the fact that σ does not change considerably with the incident angle of UV light. These observations may be explained assuming a partial melting of $P2$ films under irradiation, which is reasonable considering the low melting point ($T = 44^\circ \text{C}$) of this polymer. A change suggesting some type of phase transition was observed under polarizing microscope immediately after irradiation. It is likely that photoinduced melting of chromophore chains stimulates their self-organization in the bulk and on the surface. The chromophores on the surface of the melted film of polymer $P2$ may behave similarly to the molecules of liquid crystalline cyanobiphenyles, which prefer to align normally to the "LC-air" interface [18]. Indeed, structurally, azochromophores of $P2$ are similar to cy-

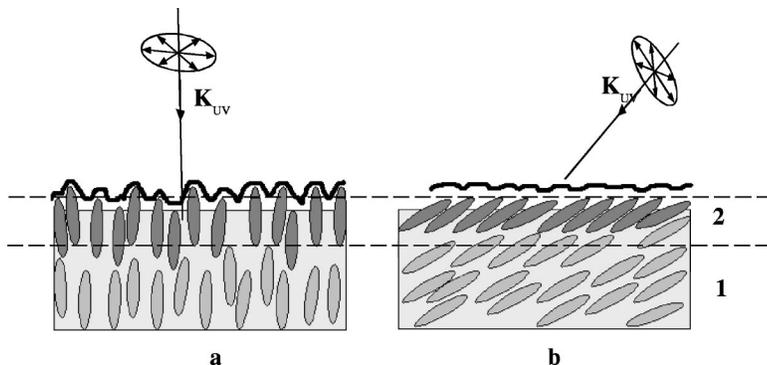


FIG. 9. Schematic representation of bulk (1) and surface (2) orientation of azochromophores in irradiated films of $P1$. (a) $\alpha_{uv} = 90^\circ$, (b) $\alpha_{uv} \neq 90^\circ$. Also, film roughness resulting from the alignment of surface chromophores is shown.

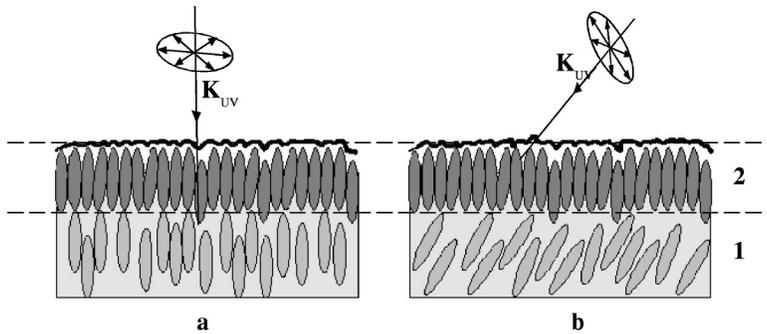


FIG. 10. Schematic representation of bulk (1) and surface (2) orientation of azochromophores in irradiated films of *P2*. (a) $\alpha_{uv}=90^\circ$, (b) $\alpha_{uv}\neq 90^\circ$. Also, film roughness derived from the alignment of surface chromophores is shown.

anobiphenyls; they both contain aromatic core with a strongly polar group on the one side and a hydrophobic chain on the other side. According to this assumption, UV irradiation stimulates assembly of azochromophores at the interface with ordering along the normal direction. The assembly at the surface of chromophores containing strong dipole groups NO_2 can be caused by the effective interaction among the aromatic cores. A possible mechanism is the $\pi\pi$ interaction accompanying the formation of H aggregates in the bulk of this polymer [19]. Such an interaction suggests a close packing of azochromophores. This process, together with possible diffusion of azochromophores from the bulk, may result in a densely packed surface characterized by reduced roughness. The structure of polymer bulk and polymer surface in the context of this concept is shown in Fig. 10. If the surface alignment of azochromophores in *P2* films is mainly governed by their intrinsic self-organization, free from any influence of the UV light as seen in polymer *P1*, it should be independent of the irradiation angle. This, indeed, agrees well with the fact that the value of σ of *P2* films does not depend on the angle of UV light's incidence.

LC alignment on *P1* and *P2* films correlates very well with the surface ordering of azochromophores. In case of *P1*, LC director tilts in the direction of azochromophores, which are oblique to the surface. One can say that LC mimics the surface order of polymer. An increase in the angle of UV's incidence leads to an increase in the tilt angle of azochromophores in the bulk and on the surface of the film which results in increased pretilt of LC. In the case of *P2*, cyanobiphenyl LCs also mimic surface order of azochromophores aligning normally to the film. The lack of dependence of the LC pretilt angle on the angle of incidence of UV light agrees with the same behavior of surface azochromophores. Poor alignment of LC ZLI 4801 on *P2* films may be explained by weak interaction of its molecules with azochromophores of *P2*.

Thus, we believe that surface packing of azochromophores determines the nature of intermolecular interactions at the interface. In *P1* polymer, containing chromophore tails with hydrophobic fragments, one can expect that surface is fairly "crumply." The free volume between azochromophores may be filled with LC molecules. Under these conditions, steric interactions between LC and azochromophores should become important. This may explain why LC of different structures exhibit similar alignment on *P1* films. By contrast, in the case of polymer *P2*, with closely packed surface azochromophores, steric factors van-

ish, whereas dispersive interactions prevail. This interaction and, hence, LC alignment, should depend considerably on the structure of azochromophores and LC molecules.

At this point, one can return to the question of correlations between orientational order of the LC and azopolymer layers with which it comes in contact. The results obtained for polymer *P1* clearly show strong correlations. In turn, these correlations are not observed for polymer *P2* having different bulk and surface alignment of azochromophores. Hence, ordering tendency can be effectively transferred from polymer bulk to polymer surface and then to LC if this symmetry is not lost at the polymer-LC interface.

It is important to discuss the role of interface topology on LC alignment. The x-ray studies reveal the anisotropy of surface roughnesses of *P1* films. The direction of lower roughness is parallel to the projection of the axis of LC alignment on to the polymer film. This conforms to the rule stated earlier for several aligning substrates [9,14,15]. The isotropic relief structure of *P2* films also correlates well with homeotropic (i.e., isotropic in the film plane) alignment of LC. These results imply that LC's anisotropic elastic interaction with the topologically anisotropic polymer surfaces may be an important factor in determining the in-plane component of LC alignment. The contribution of epitaxial and topological factors to LC alignment is one of the hotly discussed topics in LC field [20–22]. We believe that anisotropy of surface topology plays a key role in determining the direction of the in-plane LC alignment, whereas molecular interactions determine anchoring energy and LC pretilt angle.

V. CONCLUSIONS

The "azopolymer-LC" bilayer is considered as a binary system capable of mutually influencing the phases possessing "frozen" and "spontaneous" orientational order, respectively. It is shown that ordering character can be effectively transferred from polymer bulk to the polymer surface to the LC. The efficiency of this transfer is strongly determined by the order at polymer's surface, which depends on the competition between photoorientation and self-organization processes. This correlation is especially strong for the "polymer-LC" system characterized by a broad interface with interpenetrating LC and polymer components. In contrast, closely packed surface structure formed by effective

self-organization of polymer fragments (e.g., by dense aggregation of azochromophores) may destroy orientational correlation between polymer film and the LC. Thus, to effectively utilize the UV alignment method, the LC and the polymer should be carefully matched to generate desired alignment and pretilt. The results suggest an important role of the surface roughness anisotropy in determining the direction of the azimuthal alignment of LC. This agrees very well with

the conclusion drawn earlier for the alignment caused by polarized light.

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