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Anisotropic surface morphology of azopolymer films generated by polarized UV light irradiation

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X-ray reflectivity measurements reveal anisotropy of the vertical surface roughness caused by exposure to linearly polarized UV (LPUV) light in the films of two azopolymers. The irradiated surface is found to have higher roughness in the direction parallel to the direction of polarization than in the orthogonal direction. The photo-modification of the surface morphology is caused by spatial changes induced in polymer films by LPUV irradiation. The important role of surface roughness anisotropy in determining the alignment of liquid crystals is discussed.

1. Introduction

Azopolymers are excellent materials for optical data storage [1] and alignment of liquid crystals (LCs) [2]. As is commonly known, the birefringence and spectral dichroism are induced in films of azopolymers upon LPUV irradiation by the interaction of the electric field of the UV with the strong dipole moment of the azobenzene pendant groups, which is directed along their long axis. Consequently, azobenzene pendate groups undergo *trans*-*cis*-isomerization accompanied by reorientation of the azobenzene pendant groups perpendicular to the direction of the electric field **E** of polarized light. In this orientation, energy absorption by the chromophores is minimized. The orientational order of azobenzene pendant groups along this direction can also cause, to a certain degree, reorientation of the non-photosensitive pendate groups of polymer molecule, which would enhance the stability of the consequent induced order [3].

LPUV irradiation is found to influence not only the spatial orientational structure of a polymer film but also its surface topography (or morphology). Using atomic force microscopy (AFM), Rochon *et al.* [4] observed changes in the surface morphology of azopolymer films used to record intensity holograms. It was revealed that spatially modulated light intensity causes a modulation of the refractive index of the film as well as the film thickness. The amplitude of the thickness modulation was estimated to be of the order of 1000 Å (as compared with layer thicknesses of 380–1800 Å). The surface modulation was ascribed to a thermophysical mechanism arising from light absorption. Ramanujam *et al.* [5] found that relief gratings also appear in the case of the recording of polarization holograms when only the polarization direction of the light is spatially modulated. To explain the origin of surface gratings, Jiang *et al.* [6] assumed a re-aggregation of polymer chains caused by their interaction with the internal field arising from the photo-orientation of azobenzene pendant groups.

In this paper, we report the results of our study of the influence of UV light with spatially uniform intensity and linear polarization on the surface topology of azopolymer films. In contrast to the previous AFM studies, we utilized the X-ray reflectivity (XRR) method. This method allows one to determine not only the change in the surface roughness but also the thickness of the film before and after irradiation. Furthermore, XRR can be used to determine the anisotropy in the surface roughness [7], i.e. different rms vertical roughness in the two in-plane directions. Our results show that LPUV irradition increases the roughness of azopolymer surfaces and that the extent of the roughness change is different in the directions parallel and perpendicular to the direction of polarization. The roughness change in the direction of polarization is more pronounced than in the perpendicular direction. The role of the surface roughness anisotropy in determining the direction of LC alignment on azopolymer films is also discussed.

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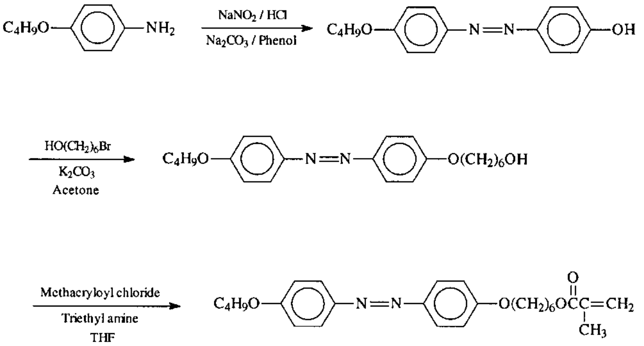
2. Experimental

2.1. *Materials and sample preparation*

We used two azopolymers with the chemical formulae shown in figure 1.

The synthesis route for the azomonomer 1 (P1), presented below, was carried out by free radical polymerization with 2,2-azobis(isobutyronitrile) initiator in a benzene solution at 60°C under nitrogen. Details of the synthesis of the azopolymer 2 (P2) were previously reported in [8].



Both materials, P1 and P2, are comb-like polymers with azobenzene pendant groups in side chains connected by a flexible alkyl spacer to the polymer backbone. The side chains in polymer P1, as shown in figure 1 (*a*), contain a hydrophobic alkyl tail $-C_4H_9$ attached to the azobenzene moiety. Side chains of the polymer P2, figure 1 (*b*), contain polar $-NO_2$ end groups. Both azopolymers have liquid crystalline properties. Polymer P1 exhibits a reentrant nematic mesophase in the interval 112–140°C; polymer P2 forms the smectic A and the nematic mesophase in the intervals 44–52°C and 52–55°C, respectively. Both polymers are solid at room temperature.

The films were prepared by spin-coating the solutions of azopolymer P1 and P2 in dichloroethane onto pre-cleaned microscope glass slides purchased from Fischer Scientific. In order to reduce the film thickness for XRR measurements, concentrations as low as 10 wt% of the polymer were spin-coated at a spinning speed of 2500 rpm. The films were dried at room temperature for two days to remove the solvent.

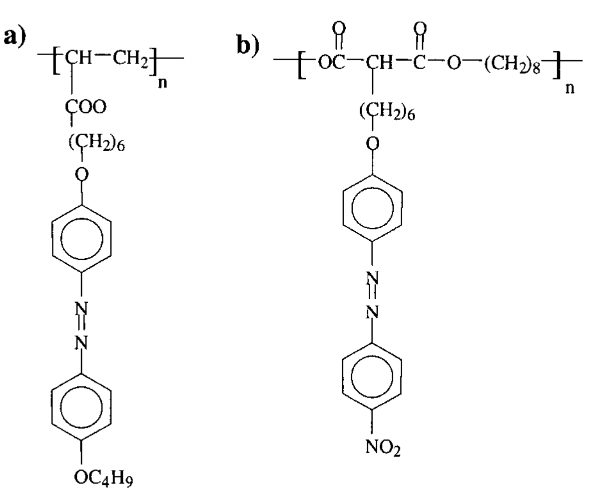


Figure 1. Structural formulae of (*a*) polymer P1, and (*b*) polymer P2.

A beam of UV light from a Xe lamp (Oriel), linearly polarized using a dichroic UV polarizer (also by Oriel), was used. The intensity of light used in our experiments was 5 mW cm^{-2}, in the wavelength range 326–400 nm.

2.2. *X-ray reflectivity*

The specular X-ray reflectivity $R(q)$ from a single air–substrate interface can be described by the Fresnel formula multiplied by a Debye-Waller-like factor [9] to account for the vertical roughness of the interface:

$$R(q) = |r_{as}|^2 = \left|\frac{q - q_c}{q + q_c}\right|^2 \exp(-qq_c\sigma^2) \tag{1}$$

where, r_{as} denotes the X-ray reflectance at the air–substrate interface, $q = (4\pi \sin\theta)/\lambda$ is the magnitude of the momentum transfer vector along the surface normal, q_c is the value of q at the critical angle, and σ is the rms value of interfacial roughness treated as a random distribution of atoms or molecules with respect to an average position of the interface.

For a film deposited on a substrate, the reflectivity is determined by the air–film and film–substrate interfaces. For a film of thickness d and with real part of the refractive index n for X-rays in the azopolymer films, the reflectivity can be written [10] as

$$R(q) = \left|\frac{r_{af} + r_{fs}\exp(inqd)}{1 + r_{af}r_{fs}\exp(inqd)}\right|^2 \tag{2}$$

where, r_{af} and r_{fs} are the X-ray reflectances at the air–film and film–substrate interfaces, respectively. The interference of waves reflected from these two interfaces generates Kiessig fringes, containing information about the film thickness, electron density gradients in the direction perpendicular to the substrate, and the rms roughnesses at the two interfaces.

The roughness of azopolymer films, before and after UV irradiation, was determined by specular XRR measurements using CuK$_\alpha$ radiation from an 18 kW Rigaku rotating anode generator and a four-circle Huber goniometer. A pair of polished Si (1 1 1) crystals were used as monochromator and analyser to achieve a high resolution of $\sim 10^{-4}$ Å^{-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 direction of UV polarization, marked as the x-direction in figure 2,

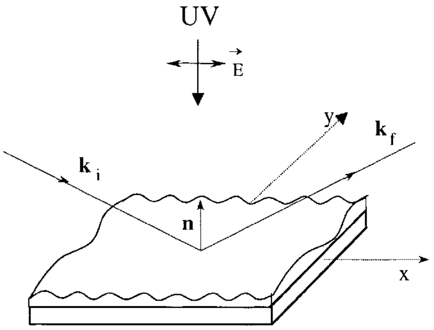


Figure 2. Sample orientation with respect to the illuminating polarized UV beam, incident X-ray beam with wavevector $\mathbf{k}_i$, and reflected X-ray beam with wavevector $\mathbf{k}_f$. **E** represents the electric field of the polarized UV beam, **n** is the surface normal, x- and y-axes are the two in-plane directions.

was confined to the X-ray scattering plane. For the second scan, the sample was rotated to bring the y-direction (which is perpendicular to the x-direction) into the scattering plane. These are referred to as the x- and y-directions or scans in our discussion below. Further description of the experimental set-up, procedure, and data anlaysis can be found in [11].

The features of the photo-induced ordering in the films of polymers P1 and P2 were previously reported in [3, 12, 13]. However in those experiments, the thickness of the films was about one order of magnitude larger than in the present study. To examine if the behaviour of thin films was different from thick films, phase retardation measurements were also carried out on the films investigated by the XXR method.

Because of the small thickness of these films, a special set-up was used for measuring the low values of the phase retardation [14]. A He-Ne laser was used in conjunction with a photoelastic modulator (PEM 90, Hinds Instruments) placed between a pair of crossed polarizers. The optic axis of the PEM was kept at 45° with respect to the axes of a crossed polarizer and analyser pair. The samples were mounted on a motorized rotation stage and placed between the PEM and the analyser, keeping the UV polarization direction perpendicular to the PEM optic axis. A collimated beam of light from the He-Ne laser was incident normal to the substrate. The signal from the photodetector placed after the analyser was fed to a lock-in amplifier tuned to a 50 kHz signal from the PEM driver. The sensitivity of this method enabled us to measure the phase retardation with a precision of 0.01°.

3. Results and discussion

Initially, the rms roughness σ of bare glass substrates in the two in-plane directions was measured from reflectivity scans performed with the substrate in x- and y-orientations. From the fit of the measured reflectivity to equation (1), the surface morphology was found to be isotropic with an rms roughness of about 3.0 ± 0.5 Å. The reflectivity scans of the non-irradiated azopolymer films in x- and y-orientations are slightly different, as shown in figure 3 for P1, suggesting that the surface roughness is slightly anisotropic. This anisotropy arises due to the flow during the spin-coating process. A fit to equation (2) gives the values of rms roughness in x- and y-directions to be 33 ± 2.0 and 28.5 ± 2.0 Å, respectively, with a roughness anisotropy of about 4.5 Å. Using the formula $d = 2\pi m/(\Delta q)$, where m is the number of fringes, the thickness d of the azopolymer P1 film was determined to be approximately 1800 Å.

The reflectivity scans for the LPUV-irradiated film of P1 are also shown in figure 3. The value of the roughness estimated for x- and y-directions are 42.7 ± 2.0 and 30.5 ± 2.0 Å, respectively. Upon comparison with the roughness values before UV exposure, it becomes evident that the roughness of the LPUV-treated film significantly increases in agreement with [15], but by different factors along the two directions. This can be clearly seen from the increased difference in the amplitude of Kiessig fringes in reflectivity scans taken in the x- and y-directions. From the data analysis, we obtain an increase in the roughness anisotropy, Δa from 4.5 to 12.2 Å. The increase in the roughness in the x-direction for P1 is 5 times larger than in the y-direction. As shown below, the LC director on these surfaces is along the y-direction; that is, along the smoother of the two directions.

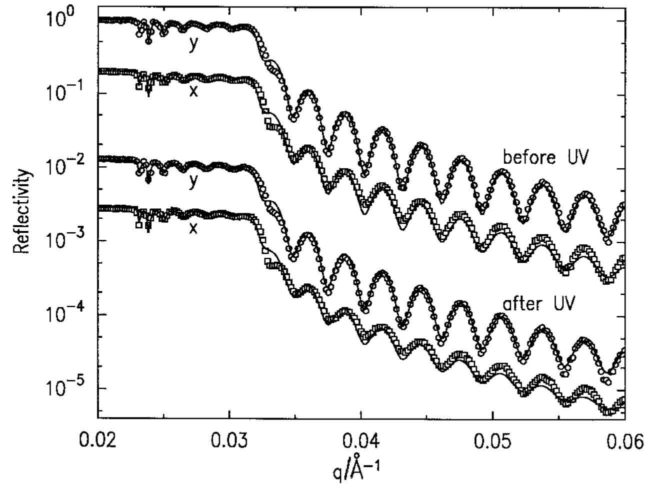


Figure 3. Specular reflectivity scans, vertically shifted for clarity, in the x- and y-directions for the film of polymer P1 before and after LPUV irradiation. Pronounced Kiessing fringes indicate film uniformity. The amplitude of interference fringes is larger in the y-direction than in x-direction for the irradiated film, indicating an anisotropy in surface morphology. Solid curves represent fits as discussed in the text.

Similar measurements on a freshly prepared 330 Å thick film of P2 yield a value of the roughness anisotropy to be approximately 4 Å. When this film is irradiated with LPUV, the roughness in the two directions increases qualitatively in the same manner as for P1. The increase in roughness in the x-direction is approximately twice that in the y-direction. This increase in the roughness and roughness anisotropy is in good agreement with previous XRR and AFM results [11] for LB films of 12-6 poly(diacetylene acid) (PDA) and spin-coated films of poly(vinyl methoxycinnamate) (PVMC).

We show the phase retardation versus rotation angle curves in figure 4 for a film of P1 before (curve 1) and after (curve 2) LPUV irradiation. A small retardation is detected even for the non-irradiated film. As stated above, this slight local anisotropy is associated with the mesogenic flow properties of azobenzene pendant groups during film preparation. Flow due to centrifugal forces during the spin coating process can cause local alignment of the polymer chain, which is responsible for the small measured surface roughness anisotropy.

Upon LPUV irradiation, the retardation of P1 films increases by a factor of ten. Surprisingly, the increase in the phase retardation of P2 film, which is nearly six times thinner, is approximately the same as for P1. This suggests that the birefringence of P1 films is about one sixth that of P2 films. It is evidence of preferential out-of-plane alignment of azobenzene pendant groups in polymer P1 and in-plane alignment for P2. This result is in complete agreement with the null ellipsometry results [12, 13] for thicker films of P1 and P2. A difference in the alignment of azobenzene pendant groups in P1 and P2 was explained [12, 13] as an intrinsic property of self-organization determined by the chemical structure of polymer molecules. LPUV exposure induces an in-plane anisotropy in both polymers via chain reorientation mechanisms. However, such reorientation does not change the preferred out-of-plane alignment of azobenzene units in P1. It is reasonable to suppose that these groups align preferentially out-of-plane for P1, inducing larger surface roughness anisotropy compared with the in-plane alignment in P2. In this manner, the larger topological anisotropy of films of P1 and of P2 can be understood.

Lastly we would like to stress the role played by the anisotropic surface topology in determining the direction of LC alignment. The LPUV-exposed azopolymer films provide excellent alignment of LCs. Alignment of LC ZLI-4801-000 was investigated in two types of cells: *symmetrical* cells constructed with both UV-exposed azopolymer surface and *hybrid* cells combining UV-exposed azopolymer and rubbed polyimide substrate. The symmetric cells were used to determine the type of orientation (i.e. homogeneous or homeotropic) while the hybrid cells were used for estimating the direction of LC alignment on the azopolymer substrate. We found that LC ZLI-4801-000 aligns homogeneously on the P2 substrates. The easy axis for LC alignment is perpendicular to the polarization of UV light **E** (figure 5). As shown above, this direction is smoother than the direction parallel to **E**. On the non-irradiated substrates of P1, the LC aligns almost homeotropically (pretilt angle ~ 90°) with random azimuthal distribution.

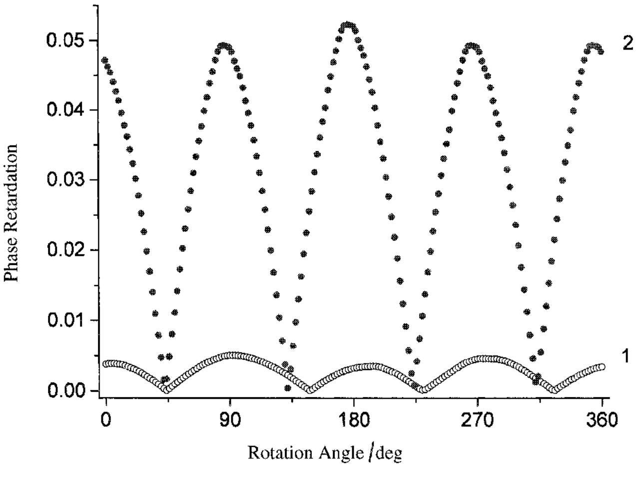


Figure 4. Optical phase retardation as a function of the rotation angle of the polymer P1 film before (curve 1) and after (curve 2) LPUV irradiation.

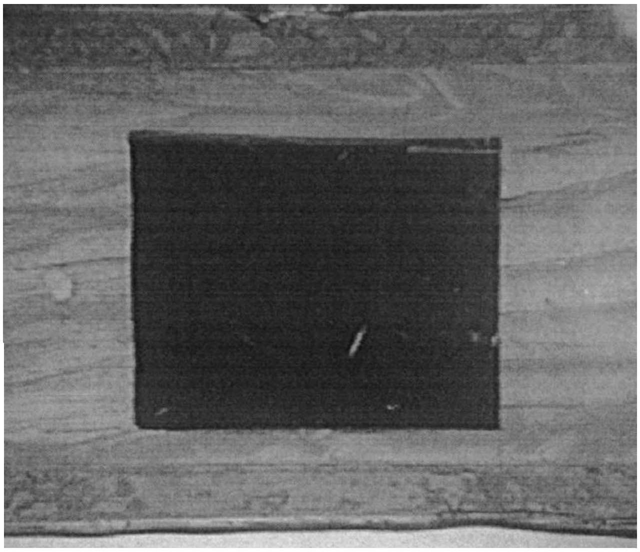


Figure 5. Photograph of the cell filled with LC ZLI 4801-000 placed between parallel polarizers. Both substrates are covered with layers of polymer P2 and have been irradiated with LPUV light. The cell is assembled with these substrates to form a twisted structure of the LC director.

The LPUV exposure of P1 substrates breaks the azimuthal degeneracy of the nearly homeotropic alignment with a tilt preference towards the direction perpendicular to **E**.

As in the case of rubbed polyimide films, the two factors likely to be responsible for the alignment are: (1) anisotropic dispersive (van der Waals) interaction of the LC molecules with the orientationally ordered polymer pendate groups; (2) anisotropic elastic properties of the LC on a topologically anisotropic polymer surface. It is difficult to distinguish the contribution of these factors in LC alignment. The influence of both factors on homeotropic LC alignment has been poorly investigated. However, the contribution of these factors in the case of homogeneous alignment has previously been studied [7, 16]. We believe that the direction of LC alignment is determined mainly by the morphological anisotropy, while the magnitude of the anchoring energy depends on the LC and polymer interaction. This inference is consistent with previous results obtained for UV-exposed PDA and PVMC films, which also align the LC in the less rough direction [7]. Liquid crystal molecules have been found to align along the direction of lower roughness in a large number of systems [16] which include mechanically rubbed as well as LPUV-exposed substrates.

4. Conclusions

To summarize, anisotropy in the vertical rms roughness (or morphology) of spin-coated azopolymer films irradiated by polarized UV light has been determined. The films are less rough in the direction of the LC alignment and the directions of alignment of azobenzene pendant groups; that is, perpendicular to the direction of polarization of LPUV. The roughness anisotropy depends on the intrinsic properties of self-organization of the polymer molecules. The topological anisotropy seems to be of major importance in determining the direction of LC alignment, while the interactions between the substrate and LC molecules determine the anchoring energy.

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