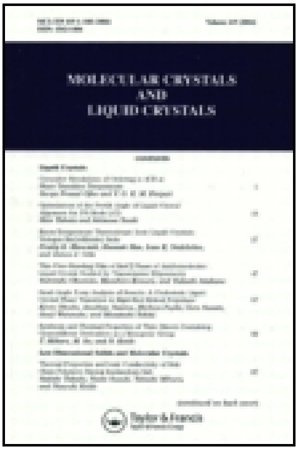

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Bulk and Surface Investigation of Photooriented Polymer Films

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The photo-generation of optical anisotropy is investigated in spin-coated films of two liquid crystalline polymers containing differently substituted azobenzene side groups upon irradiation with linearly polarized light. UV spectroscopy with polarized light, waveguide spectroscopy and NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy have been used to characterize the photoinduced order within the film and at the surface. While azimuthal anisotropy is observed in the volume of both polymers, surface anisotropy is only found in case of the homopolymer. The azobenzene moieties of the copolymer do not show any out-of-plane orientation at the surface.

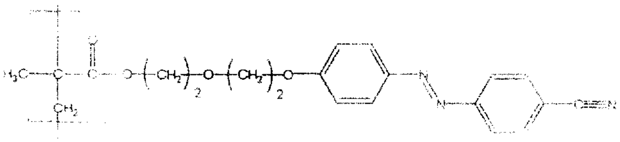
Keywords: photoorientation; photoisomerization; azobenzene; side chain liquid crystalline polymer; NEXAFS spectroscopy; surface; photoalignment

INTRODUCTION

Anisotropic polymer films of photochromic liquid crystalline polymers formed by exposure to linearly polarized light have received an increased technological attention for optical data storage, producing of optical components, and for photoalignment of liquid crystals. In contrast to rubbed polyimide surfaces [1-2], photoselection and photoorientation processes open the possibility to induce anisotropy by light [3], which allows a local control of the aligning direction. The photoorientation of azobenzenes has been investigated in different types of films and materials [3, 4-6]. It was shown that the initial order and the history of the films have a strong influence on the orientation process. The studies are representative for bulk films of some hundred nm to some µm. However, we have no information about the photoorientational behavior at the surface. A key function for understanding of photoalignment processes exists in the anisotropic properties of the photooriented polymer surface and in the interactions between the polymer surface and the liquid crystal. Therefore, the photoinduced order of the chromophores within the polymer film was studied by UV-VIS spectroscopy with polarized light, and the orientation at the surface of the films was detected by NEXAFS spectroscopy.

EXPERIMENTAL

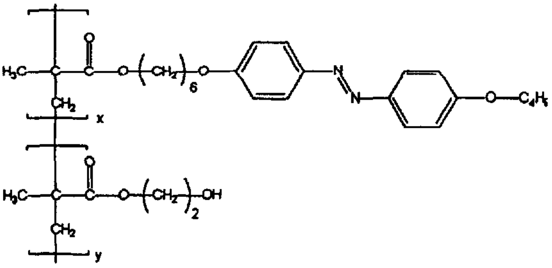
Two liquid crystalline polymethylmethacrylates containing the 4-alkoxy-4'-cyanoazobenzene unit (homopolymer (I): g 58°C LC 115°C i) or the 4-alkoxy-4'-butoxyazobenzene group (copolymer (II) with 29 % azobenzene group content: g 63°C LC 118°C i) were used for the experiments



(I)

Films with a thickness of either 0.1 µm (I) or 250-300 nm (II)

were prepared by spin-coating on glass substrates using a solution of 10 mg of the liquid crystalline polymethylmethacrylates in 1 ml THF.



(II)

In case of the homopolymer (I), the 488 nm line of an Ar^+ laser (50 mW/cm^2) was used for the irradiation experiments. The film of the copolymer II was irradiated with non-polarized light (365 nm, 0.5 mW/cm^2, 30 min). In a consecutive step, the same film was irradiated with an Ar^+ laser (57 mW/cm^2 at 457 nm for 30 min).

Polarized UV-VIS measurements were carried out with a diode-array spectrometer (Polytec XDAP V2.3) to determine the in-plane order of the films. A computer-driven stepper with a polarizer was taken for polarized investigations. The order parameter (S) of the entire polymer film was calculated as $S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$.

The three-dimensional refractive indices were determined by waveguide spectroscopy using a He-Ne laser (632.8 nm). The films were 2.1 μm (homopolymer (I)) and 3.7 μm (copolymer (II)) thick and obtained by spin-coating from THF (I) and chloroforme (II) solutions.

The determination of the film surface orientation was carried out by NEXAFS measurements under ultra high vacuum conditions (base pressure below 5×10^{-10} mbar) at the beamline HE-TGM-2 of the Berlin synchrotron radiation facility BESSY I. A home made NEXAFS detector based on a double channel plate (Galileo) was used with a resolution of $E/\Delta E = 580$ [7]. The spectra were recorded in the partial electron yield (PEY) modus with a retarding voltage of −150 eV to reduce inelastic scattered electron contributions for an increase of the surface sensitivity. Simultaneous recording of the flux of the incident radiation (I_0 signal) was realized by using a gold grid. Monitoring of the flux allowed a calibration of the exact energy position of the monochromator. The data obtained were normalized to a constant incident photon flux. Therefore, a constant background was subtracted, and the spectra were divided by a spectrum, which was recorded from a freshly sputtered Au wafer. The surface structure of the copolymer film was investigated using the AFM (Atomic Force Microscopy) Topometrix equipment.

RESULTS AND DISCUSSION

As shown in Fig. 1 and 2, the initial state of the films of both polymers are in-plane isotropic after spin-coating. This result agrees well with the results of waveguide spectroscopy. Waveguide spectroscopy indicates a small out-of plane orientation in case of the homopolymer, whereas the copolymer was found to be slightly in-plane oriented (Table 1).

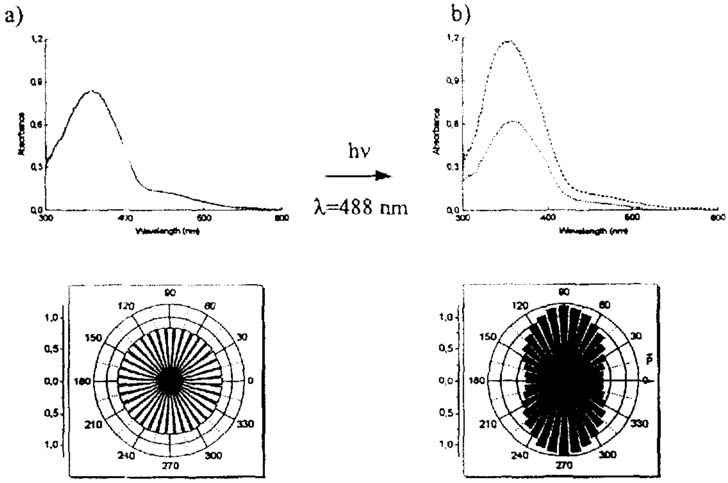


FIGURE 1: Polarized UV/VIS spectra of the homopolymer (I) film parallel and perpendicular to E of the laser light and the corresponding polar plots at the maximum of absorbance, a) after spin-coating, b) after Ar^+ laser irradiation (488 nm, 1h, 50 mW/cm^2).

The irradiation with linearly polarized light (488 or 457 nm) results in an orientation of the azobenzene side groups perpendicular to the electric field vector E of the incident laser light. The irradiation experiments were carried out in normal incidence and at room temperature, where both liquid crystalline polymers are in the glassy state. However, there is no information about the thermal properties at the surface.

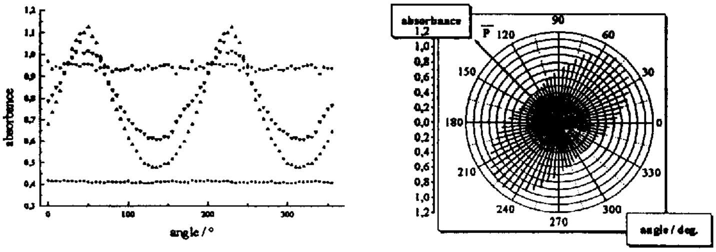


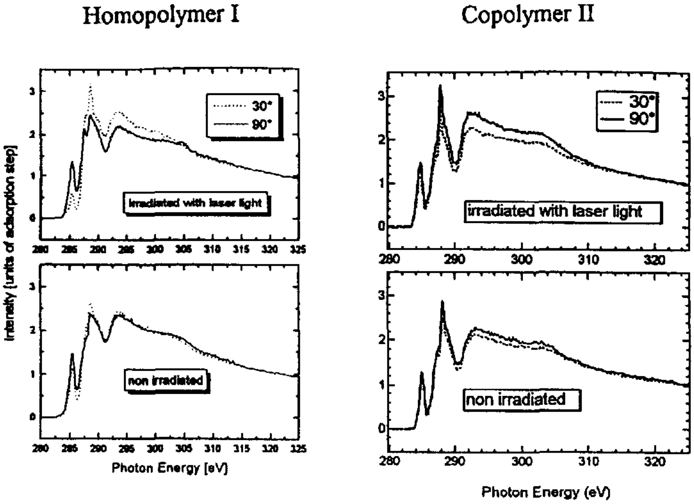
FIGURE 2: Angular-dependent absorbance of the copolymer (II) film after spin-coating (□), after UV irradiation (365 nm, 0.5 mW/cm^2, 30 min) (•) and polarized irradiation (457 nm, 57 mW/cm^2, 30 min) (Δ), after several weeks of relaxation (∇)

The parameter S obtained by polarized UV-VIS measurements at the maximum of the π-π* transition of the azobenzene group results in a value of 0.22 after polarized irradiation. So, the azimuthal or in-plane anisotropy is found to be comparable for both polymers. A dichroism of S = 0.31 was induced by polarized irradiation, which slightly decreases (S = 0.19) after storage at room temperature for several weeks.

TABLE 1: 3D spatial order in the bulk film detected by waveguide spectroscopy. (irradiation with 488 nm for 12 h).

	n_x	n_y	n_z	
sc film (I)	1.654	1.652	1.658	slightly out-of-plane
irr. 2.16 kJ/cm²	1.610	1.696	1.679	oblate
sc film (II)	1.575	1.576	1.564	slightly in-plane
irr. 3.80 kJ/cm²	1.534	1.603	1.587	oblate

The NEXAFS spectra of the homopolymer (I) films measured at different angles in relation to the substrate are plotted in Figure 3. The π* resonance at about 285 eV is assigned to an excitation of an inner core electron into the LUMO (1s → π*) and exhibits a maximum for spectra recorded at normal incidence (90°). The tilt angle between the π* orbital and the surface normal was obtained with an accuracy of ± 2° as described in the literature [8]. A quantitative analysis of the π*-resonance intensity yields an average tilt angle of the transition dipole moment of 61° for the non-irradiated homopolymer (I) film indicating a slightly out-of plane orientation of the chromophores at the surface. This corresponds to the results of the waveguide spectroscopy, whereas this method and the UV-vis measurement show that the sample is azimuthally isotropic. Irradiation of the homopolymer (I) film results in an increase of the average tilt angle of the π*-resonance intensity for the transition dipole moment to 74°, which indicates an upright orientation of the phenyl rings. Furthermore, a large dichroism was found in case of the irradiated homopolymer film for the resonance at about 289 eV (Figure 3), which could be similarly assigned as a Rydberg resonance (R*) [9]. The quantity R* allows to determine the orientation of hydrocarbon chains. Furthermore, the strong dichroism of the irradiated homopolymer film indicates the cooperative effects between the chromophore in the side chain and the aliphatic chain segments existing in the side chain and in the main chain during the orientation process. The results agree with the waveguide measurements, which indicate a decrease of the refractive index parallel to E (n_x) and an increase in the direction perpendicular to E (n_y) and in the propagation direction (n_z) For both polymers an oblate order ($n_z \approx n_y > n_x$) is found.


Homopolymer I

Copolymer II

FIGURE 3: NEXAFS spectra at the K-edge of the polymer films after Ar^+ laser irradiation (top) in comparison to a non-irradiated film (bottom) for the homopolymer (I) and the copolymer (II).

The results for the surface orientation obtained by using the copolymer (II) differ from those found for the homopolymer (I). UV measurements show a dichroism in case of the irradiated film whereas just a slight dichroism was found for the non-irradiated film. In contrast to the results of UV-vis measurements, NEXAFS spectra do not show these dichroic differences between the non-irradiated copolymer film and the film irradiated by laser light. This result indicates clearly that the surface of the copolymer (II) film does not show significant out-of-plane changes by polarized irradiation. Several reasons can be discussed for this result. Firstly, the spacer length of the side chain containing the chromophore is higher in comparison to the spacer length of the other comonomer unit in the copolymer (II). Secondly, the mobility of the chromophore is considerably higher at the surface of the copolymer (II) film in comparison to the homopolymer (I) film, which may be contributed to the copolymer (II) structure. Thirdly, hydrogen bonding between the hydroxyl group and any other polar group existing at the polymer surface may have a pronounced influence on the orientation process at the surface in comparison to the photoprocesses occurring in the bulk material. In addition, AFM investigations of the copolymer (II) films indicate changes at the surface contributed to the irradiation with laser light. The average surface roughness calculated from AFM decreases from 12.9 [Å] for the spin-coated film to 5.4 [Å] for the irradiated film. The smoothing of the surface is contributed to the irradiation with laser light.

CONCLUSION

The results indicate that waveguide spectroscopy is a powerful tool to characterize the 3D spatial order of bulk film while NEXAFS spectroscopy allows to characterize the surface anisotropy. The comparison of the results between NEXAFS and conventional spectroscopy (UV-VIS, FTIR) demonstrates the specific influence of surfaces on photoreactions and photoorientation processes. In case of the copolymer, a significant photoinduced anisotropy in the bulk is found while no out-of-plane orientation of the azobenzene moieties exists at the surface. In the case of the homopolymer a comparable development of the bulk and the surface anisotropy was found.

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