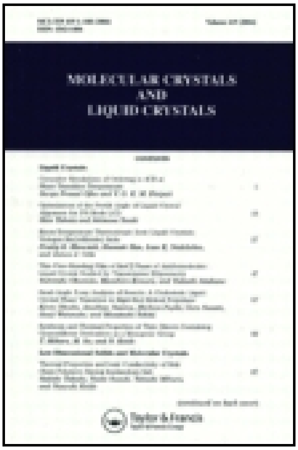

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Light Induced Modifications of Langmuir-Blodgett-Multilayer Assemblies Containing Amphotropic Azocopolymer

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LIGHT INDUCED MODIFICATIONS OF LANGMUIR-BLODGETT-MULTILAYER ASSEMBLIES CONTAINING AMPHOTROPIC AZOCOPOLYMER

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Abstract Photochromic LB-multilayers of amphotropic copolymers having rod-like azobenzene moieties as side groups which exhibit thermotropic liquid crystalline behaviour in the bulk have been characterized by UV-VIS spectroscopy as well as by angular dependent and energy dispersive SAXS. Upon irradiation with UV-light the initial optical in-plane anisotropy and the vertical layered structure of LB-films can be destroyed. A new layered structure can be rebuilt on irradiation with visible light or by annealing. Using linearly polarized light for the irradiation an optical anisotropy (POA) has been induced or reversibly modified by a photoselection process.

INTRODUCTION

Photochromic multilayers of amphotropic copolymers with rod-like azobenzene moieties as side groups which exhibit liquid crystalline behaviour in bulk show interesting changes of the supramolecular structure on annealing[1] and on irradiating[2] as well as interesting optical properties. The modification of orientation and order by means of linearly polarized light has been recently investigated in LB-multilayers[3-7] films of amorphous[8,9] as well as liquid crystalline polymers[10,11]. The aim of our paper is to study the influence of irradiation wavelength and polarization conditions on the vertical and in-plane order of LB-films built up by an amphotropic and photochromic copolymer.

EXPERIMENTAL

Photochromic Langmuir-Blodgett-multilayers containing amphotropic copolymer (fig.1) which exhibit thermotropic liquid-crystalline behaviour in bulk were prepared by means of the Langmuir-Blodgett-Kuhn (LBK) technique[12]. Stable monolayers were prepared at 20.7°C in a KSV 5000 trough on pure water (Milli-Q-system) by spreading a 10^{-3} M $CHCl_3$ solution and extremely slow compression at about 5cm^2/min. Surface pressure reading was performed with a Wilhelmy plate. Transfer of the monolayers onto hydrophobic quartz plates was carried out with a dipping speed of 5 mm/min at a surface pressure of $P_0=36$ mN/m. Transfer ratios were on the down-stroke as well as on the up-stroke $>$ 0.94. To keep the dark adapted material in the trans-configuration care was taken by working in the absence of actinic light. Polarized UV-vis spectra were measured on a PERKIN-ELMER Lambda 19 spectrometer containing a self-designed construction kit to perform a 360 degree angle scanIrradiations were carried out by a mercury HBO 500 lamp on a conventional optical desk as well as by an INOVA90 Ar^+ laser system (COHERENT) at 365, 457,4 and 488 nm respectively.

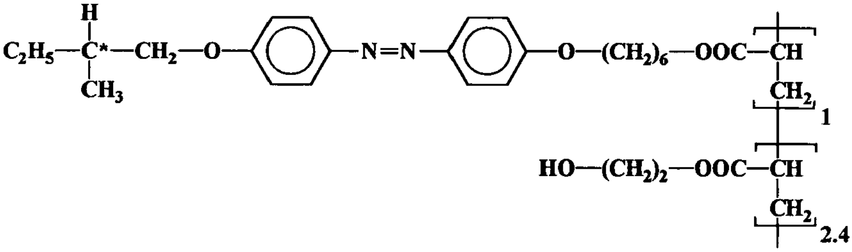

FIGURE 1 Amphotropic Azocopolymer **1**

Angular-dependent SAXS were carried out on a STOE Θ–Θ-refractometer; the energy-dispersive SAXS were performed by means of a Si(Li) detector (SILENA). Fixing the samples was done with the help of a HUBER-goniometer, the X-ray source was a 2kW Mo-tube (SIEMENS).

DISCUSSION

Absorption spectra of LB-film samples of **1** (fig.2) show the original optical anisotropy in dipping direction. The tilted layered structure corresponds to an inhomogeneous crystalline packing with a layer spacing of 45Å.

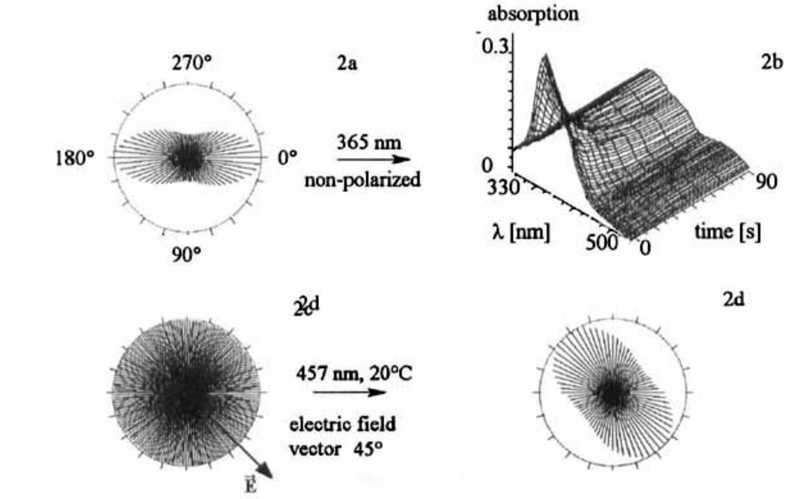

FIGURE 2 Polar spectra of **1** (2a) and 3-D-irradiation spectra (2b)of **1** at 365nm, 1.62 J/cm^2 and the corresponding polarscan (2c).Upon irradiation with polarized light (45°, 457nm) an optical anisotropy has been induced (2d).

On irradiation with non-polarized light at 365 nm a decrease of the original optical anisotropy down to zero as well as the total disappearance of the initial layer structure was observed (fig.2). Annealing the film into the "liquid-crystalline like" state at 63°C a new layered structure of 55Å appears; the sample is optically isotropic. The illumination of samples of **1** in the "LC-like" state at 63°C with polarized light at 457,4 nm results in a photoinduced optical anisotropy perpendicular to the polarization plane of the actinic light beam after allowing the sample to cool fast to room temperature. Heating back the sample to 63°C for 30 min the POA disappears while the layer spacing remains unchanged at 55Å (fig.3a).

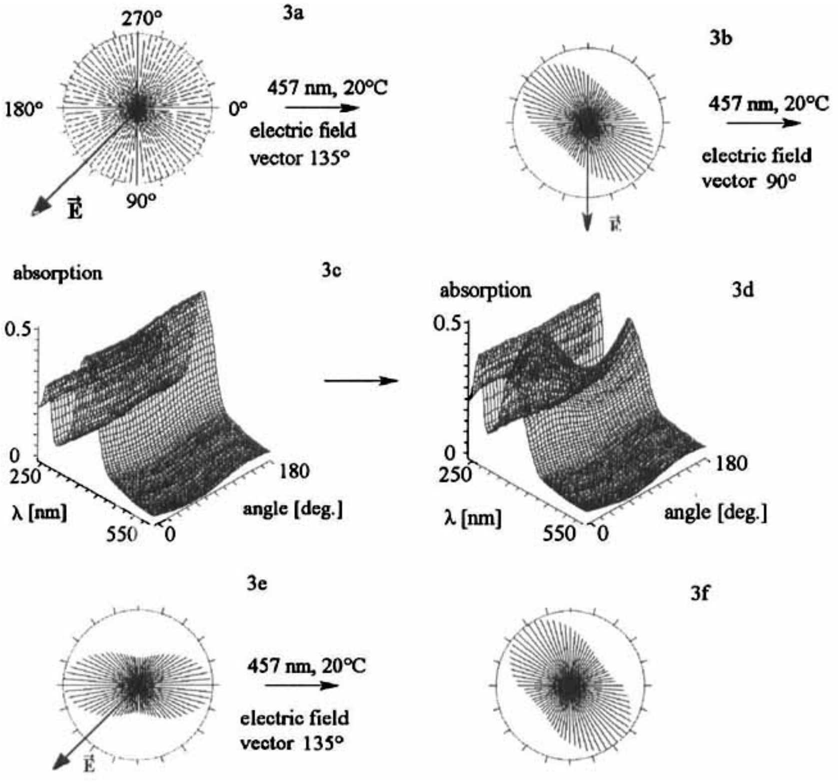

FIGURE 3 Polarscans and angular dependent spectra of the film after annealing (3a,c) and polarized irradiation (1.18 J/cm^2, 457,4 nm, 20°C, electric field vector 135°, 3b,d). On continued irradiation the POA has been switched caused by different field vectors (90° and 135° respectively, 1.18 J/cm^2, 20°C, 3e,f). Final states after irradiation were monitored in polar diagrams, electric field vector of polarization is simultaneously indicated.

The samples were irradiated at the same conditions as described above to give the original state (see 2d) and then allowed to cool to room temperature. Continued irradiating (457 nm with 1.18 J/cm^2 at 20°C) was carried out with a polarization plane of 135° (fig.3b,d). The reorientation process below glass transition at low intensities of actinic light beam results in an optical anisotropy in 45° direction which is perpendicular arranged compared with the anisotropy shown in fig.2d. Further changes in the direction of the electric field vector of light lead to a switching process of the direction of optical anisotropy in the film (fig.3e,f).

These structures are stable at room temperature; the decrease of POA within 72 hrs amounts to about 10%.

CONCLUSIONS

Amphotropic polymers combine amphiphilic and thermotropic liquid crystalline properties in the same molecule to give the opportunity for different kinds of self-organizing principles within the system. Thus, vertical layered structures can be achieved either by LBK-techniques or by selforganization of formanisotropic moieties in liquid crystalline smectic states. A reversible thermal transition occurs in LB-films of studied polymer leading to less ordered states at the same temperatures like in polymer bulk for the phase transition from crystalline to liquid crystalline state. The azobenzene moieties have been used to act as mesogenic side groups in the system. An alkyl chain as a spacer connects the rigid formanisotropic group with the acrylate backbone and in this way with the nonmesogenic and hydrophilic comonomers. The spacer allows sufficient conformational motion for the mesogenic units to form stacks of liquid crystalline states.

The light induced changing of the geometrical shape established by the different steady states at 365 and 457 nm causes a reversible structural response of the layered LC-state and lower ordered states respectively. However, the initial stressed and tilted LB-multilayer assembly can nevermore obtained back by means of actinic light and heating as well.

Upon irradiation with linearly polarized light of 457 nm optical anisotropy has been induced by an angular-dependent photoselection process. The photochromic side groups have been oriented perpendicularly to the plane of electric vector of actinic light. By this way dichroism has been induced in the film. However the layered structure of the LC-film remains constant.

The process takes place above and below glass transition temperature as well as at different light intensities. The light induced optical anisotropy (POA) can be frozen in at room temperature and remains stable for a longer period. In this way the E-Z isomerization of azobenzene moieties modifies the vertical layered structure as well as the in-plane anisotropy of LB-films by wavelength and polarization dependent irradiation.

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