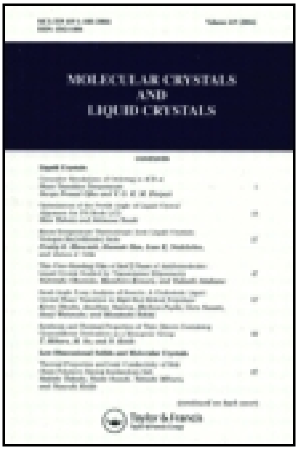

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Langmuir-Blodgett Films of Photochromic Polyglutamates: Structures and Photochemically Induced Structural Changes

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Langmuir-Blodgett Films of Photochromic Polyglutamates: Structures and Photochemically Induced Structural Changes

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Abstract Attachment of azobenzene moieties, substituted with alkyl chains, to a polyglutamate backbone give photochromic "hairy rod" polymers, capable of forming monolayers at an air/water interface. These monolayers can be transferred to substrates as Langmuir-Blodgett films. Irradiation and concomitant photoisomerization of the chromophore result in structural changes of the monolayers and the LB films, which give the systems interesting photoresponsive properties.

INTRODUCTION

Rigid rod-like polymers decorated with flexible side chains, so-called "hairy rod" polymers, are a new class of monolayer forming materials /1/. The monolayers of these polymers can be transferred to substrates as very homogeneous and highly anisotropic films using the Langmuir-Blodgett technique /2/. Because of the low concentration of defects and the high stability of the LB films they are of great interest for optoelectronical applications /3-5/. In order to obtain light sensitive materials, we have combined these special architecture polymers with a photochromic dye. The polyglutamate backbone used in our investigations is a rigid rod because it winds to an α-helix which is stabilized by hydrogen bonds. Azobenzene equipped with an alkyl tail was attached to this backbone using spacers of different length. The synthesis and characterization were described in a previous paper /6/. The azobenzene moiety was chosen because the dipole moment and molecular structure can be altered by photoisomerization. With specific treatment, samples with different isomeric composition can be achieved. Storage in the dark ensures full trans (E) configuration (samples called "new"). By irradiation with an appropriate wavelength, two different photostationary states can be reached: a state "cis" (approx. 90% Z-isomer) by irradiation with UV light (high pressure Hg lamp, band pass filter, $\lambda = 360 \pm 50$ nm) and a state with a low content of Z-isomer (approximately 10%, called "trans") by irradiation with visible light /6/ (high pressure Hg lamp, cut off filter, λ > 470 nm). In this paper we will describe the structural changes which occur as a response of the photoisomerization in the monolayer and the LB film of the photochromic polyglutamates.

RESULTS AND DISCUSSION

Surface pressure/area isotherms can be used to investigate the molecular arrangement of the molecules in the monolayers. In order examine wether the content of Z-isomer has an influence on the arrangement, differently pre-treated solutions were used for spreading. It can be seen from fig. 1 that the solution stored in the dark ("new") gives the monolayer with the lowest area per monomeric unit. With an increasing amount of Z-isomer the area per monomeric unit increases, while the pressure at the collapse, which is an indication of the stability of the monolayer, decreases. This behaviour can be explained taking into account, that the Z-azobenzene moiety is more hydrophilic than the E-isomer. The Z-isomer can interact with the water surface, resulting in a less compact and less stable monolayer (see schematic fig. 1). On the other hand the E-azobenzene does not interact with the water surface and additionally it can adopt a more compact arrangement because of its molecular structure.

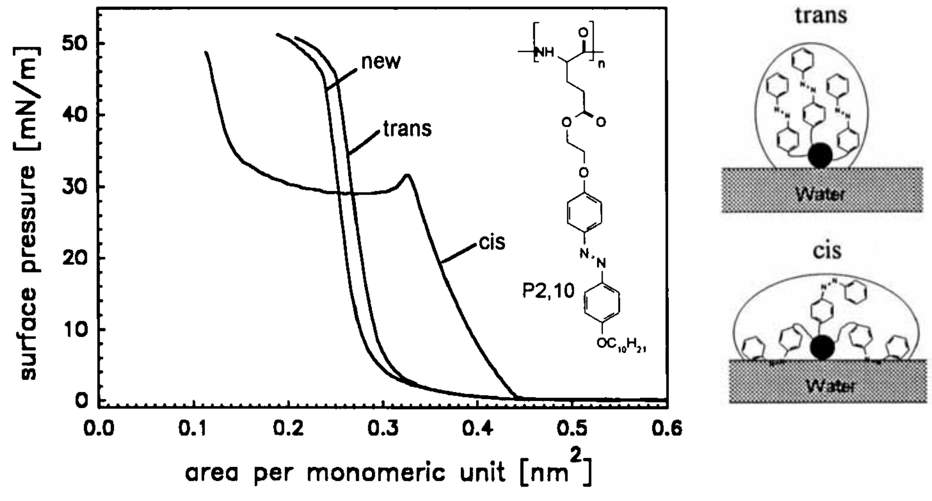
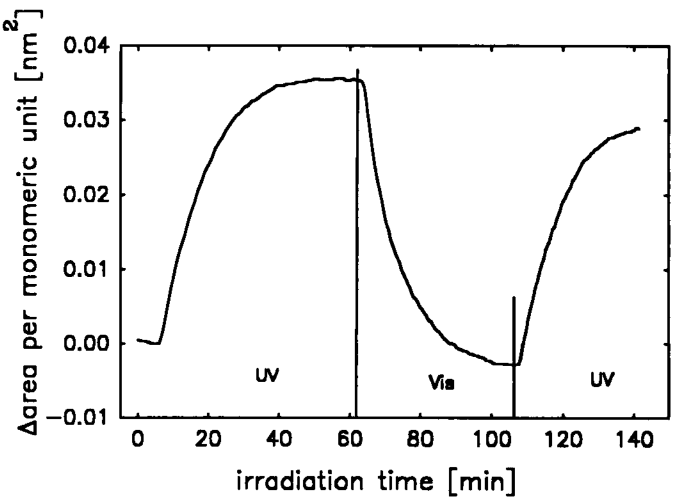


Fig. 1: Surface pressure/area isotherms of monolayers of P2,10 with different amounts of Z-isomer ("new": 0%, "trans": approximately 10%, "cis": approximately 90%) and schematic of the molecular arrangement

Depending on the amount of chromophores as Z-isomer, the molecules adopt different arrangements in the monolayer when spread from solution. In order to investigate if there are some rearrangements when the amount of Z-isomer is changed in the monolayer, a monolayer spread from a solution kept in the dark and compressed to a constant surface pressure was irradiated with UV light. As can be seen in fig. 2, UV irradiation and concomitant photoisomerization (E → Z) result in an increase of the area per monomeric unit (after an short induction period). Therefore the isomerization proceeds within the monolayer and results in a rearrangement of the molecules. This effect is reversible with irradiation of Vis light the area per monomeric unit decreases and can be repeated with subsequent UV irradiation the area increases again /7/. This expansion upon irradiation against a constant surface pressure can be used to transform light into mechanical energy.

Fig. 2:
Change in the area per monomeric unit for a P2,10 monolayer upon irradiation with UV and Vis light as function of the irradiation time



The structure of the LB films which can be obtained from the monolayers of the photochromic polyglutamates, were investigated by means of x-ray diffraction and spectroscopic methods. The structure is characterized by bilayers composed of deformed "hairy rods" (see schematic fig. 1) /8, 9/. The deformation of the "hairy rods" is a result of the interaction of the more hydrophilic polymer backbone with the water surface and the applied surface pressure. This structure is changed irreversibly when the azobenzene moieties are photoisomerized to the Z-isomer by irradiation with UV light. After an irradiation cycle, including UV and subsequent Vis irradiation, the deformed "hairy rods" relax to a more symmetrical distribution of the side chains around the main chain helix. This relaxation is associated with a loss of the layered structure and reorientation of the chromophores in respect to the main chain helix /8, 9/. The structural changes result in changes of the optical properties of the LB films, which despite the small thickness (≈32 nm), can be detected by means of surface plasmon microscopy /3/, as can be seen from fig. 3. This effect is still under investigation and will be subject of a forthcoming paper. It can be used to obtain images by irradiation of the LB film (e.g for optical data storage).

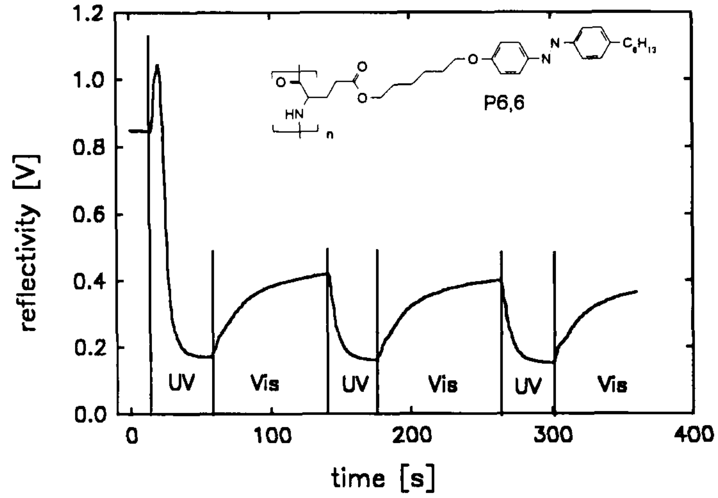


Fig. 3: Reflectivity of a glass / metal interface covered with 12 layers of P6,6 in a surface plasmon experiment as function of the irradiation time at the first and subsequent irradiation

CONCLUSIONS

The photochromic polyglutamates are light sensitive materials: The area per monomeric unit occupied by the polymers in the monolayer can be changed by photoisomerization. This change is reversible and can be repeated. The effect of expansion upon irradiation can be used to convert light into mechanical energy. Within the LB films there are structural changes upon irradiation resulting in changes of the optical properties of the films, which can be detected by surface plasmon microscopy and used for optical data storage (at least in a laboratory set-up).

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