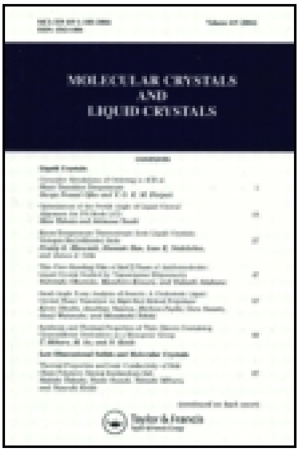

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Change in the Orientational Distribution of Non-Isomerizing Diphenyldiacetylene Chromophores in LB-Films

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LB-films of an amphiphile containing diphenyldiacetylene moieties as chromophore have been prepared. Compared to the solution the LB-films show a different intensity ratio between the two diacetylene bands in the UV/Vis spectrum due to the dense packing of the chromophores. Irradiation with polarized light at 360 nm causes an angle dependent increase in the absorbance in the π-band region, which previously has been interpreted to be due to a photoreorientation process. However, a decrease of the π'-band in the UV/Vis spectra and the C≡C vibration band in the grazing angle reflectance IR-spectra indicate a photoreaction of the chromophores, which nature remains elusive. The increase in absorbance in the π-band region is conjectured to be to partial reversal of the intensity ratio changes due to a less dense packing of intact chromophores. From experiments, in which the irradiated LB-film is dissolved, the amount of reacted chromophores can be estimated to less than 20%.

Keywords: Diphenyldiacetylene; Photoreorientation; LB-Films; Polyelectrolyte; Polarized Irradiation

Introduction

For several chromophores i.e. azobenzene polarized irradiation results in a photoreorientation of the chromophores [1, 2] and, therefore, in a change of the optical properties. This process has been suggested for applications in optical data storage, for command surfaces, or for non linear optical (NLO) effects [1, 3 - 6]. For azobenzene and other isomerizing dyes a mechanism for the photoreorientation process is widely accepted [1, 7]. Azobenzene undergoes an isomerization when irradiated with light of appropriate wavelength and the thermodynamically more stable trans isomer is converted to the cis isomer. The isomerization is reversible and the transition from cis to trans may result in an angular orientation of the chromophore different from the original one. Only those chromophores can be isomerized which have there long axis parallel to the polarization plane of the incident light. Therefore, with every isomerization cycle some chromophores are reoriented. By repeated cycles a new orientational distribution of the chromophores is established. This mechanistic model cannot be transferred to other chromophores which do not isomerize. However, in LB-films diphenyldiacetylenes show changes in their optical properties upon polarized irradiation, although the chromophore cannot be isomerized [8]. It was proposed that the chromophores are reoriented due to their interaction in the excited state with the highly ordered packing [8, 9].

For a detailed investigation of the processes taking place in LB-films containing diphenyldiacetylene as chromophore we synthesized the amphiphile 6-(4-(4-(4-hexylphenyl)butadiyne)phenoxy)hexanoic acid (DPDA) [10]. The amphiphile forms well defined and stable monolayers when spread on a subphase containing poly(ethyleneimine) (PEI). The DPDA/PEI complex monolayers can be deposited as Langmuir-Blodgett films [10].

Experimental

The amphiphile was spread from $CHCl_3$ solution on a Lauda FW 1 trough filled with a solution of poly(ethyleneimine) (PEI; Aldrich) in ultra pure water at 20°C. The concentration of PEI in the subphase was adjusted to 4.3 mg/L, which corresponds to a concentration of 10^{-4} mol/L of amine groups. UV/Vis spectra of the monolayers at the air/water interface and the LB-films were recorded on a TIDAS spectrometer (J&M, Analytische Meß- und Regeltechnik, Aalen, Germany), as has been previously described [11]. FT-IR-Spectra were obtained on a Bruker IFS55 instrument equipped with a fixed angle (85°) reflection accessory. DPDA/PEI complex monolayers were deposited onto hydrophobic quartz slides (Hellma, Suprasil fused silica optical windows) or aluminum coated glass slides at a surface pressure of 15 mN/m and a dipping speed of 2.5cm/min. Irradiation was carried out employing a

200 W high pressure mercury lamp (Oriel) with band pass filter (UG-1, Spindler and Hoyer) for light with a wavelength of 360 nm ± 50 nm. The light was polarized with a Glan-Taylor polarizer to be 45° to the dipping direction.

Results and Discussion

Synthesis and monolayer behavior of the diphenyldiacetylene containing DPDA have been described previously [10]. DPDA monolayers at the air/water interface can be stabilized by the presence of poly(ethylene-imine) (PEI) in the subphase. This effect arises from the formation of a stable complex between the anionic amphiphile and the cationic polyelectrolyte at the air/water interface.

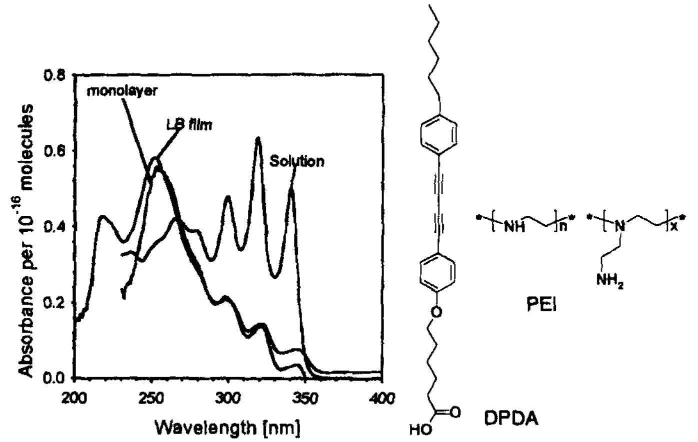

FIGURE 1: UV/Vis spectra of a DPDA solution (in $CHCl_3$), a DPDA/PEI complex monolayer (Π = 15 mN/m) and a DPDA/PEI complex LB-film

UV/Vis spectra of diphenyldiacetylene derivatives show two characteristic absorption bands at 270 nm and between 300 - 350 nm (see FIGURE 1). They belong to the two electronic systems which are perpendicular to each other [12, 13]. The absorption band between 300 and 340 nm is due to an electronic transition between π orbitals delocalized over the diacetylene moieties and the phenyl rings. This band shows considerable vibrational splitting [12]. Perpendicular to this πsystem is the π'-system of orbitals delocalized over the diacetylene moiety only. This π'-system gives rise to an absorption band at 270 nm. Both transitions are polarized along the longer molecular axis [13].

Comparison of the UV/Vis spectra of DPDA in solution and of DPDA/PEI complex monolayer of reveals significant differences in the relative intensity of the absorption bands for the π- and π'-systems (see FIGURE 1). These changes of the relative intensities in UV/Vis spectra can be ascribed to interactions between the π- and π'-systems in the solid state and indicate a dense packing [10, 12, 13].

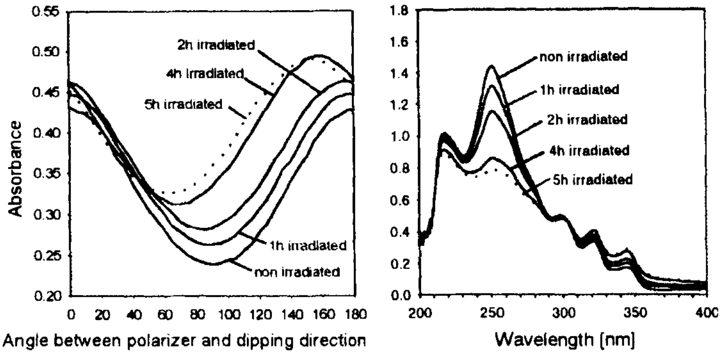

FIGURE 2: Angle dependent absorbance at 320 nm and UV/Vis spectra as function of the irradiation time for a DPDA/PEI complex LB-film

If the LB-film is irradiated with polarized light at 360 nm the spectra change significantly (see FIGURE 2). In particular there is angular dependent increase in the absorbance at 320 nm (π-band). This increase has been previously ascribed to a photoreorientation of the chromophores, since the absorbance at the new mean direction is higher for the irradiated samples than for the non-irradiated samples [8, 10]. However, the irradiation also causes a strong decrease of the π'-band absorbance (at 250 nm), which is not in accordance with a photoreorientation mechanism, unless an out-of-plane reorientation is assumed. In order to check this, we have performed grazing angle incidence FT-IR spectroscopy, which probes for vibrations with a transition dipole perpendicular to the surface. If there is an out-of-plane reorientation of the chromophores we would expect a strong increase for the $C{\equiv}C$ vibration upon polarized irradiation. As can be seen from FIGURE 3 this is not the case, but the $C{\equiv}C$-band decreases and completely vanishes after 3h of irradiation. Therefore, out-of-plane reorientation can be excluded as cause for the decrease in the π'-band absorbance, but a destruction of some $C{\equiv}C$-bonds by a photoreaction has to be assumed.

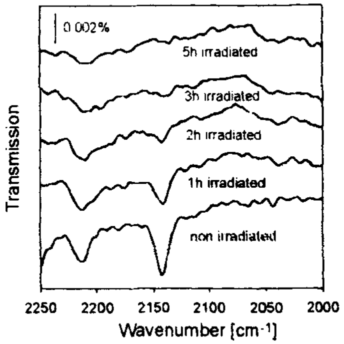

FIGURE 3: Grazing angle incidence FT-IR spectra in the $C{\equiv}C$-band region as function of the irradiation time for a DPDA/PEI complex LB-film

The extent of the photoreaction can be estimated by experiments in which the LB-film is dissolved in chloroform after the irradiation. Quantitative analysis of the solution by UV/Vis spectroscopy reveals that more than 80% of the chromophores are intact. Furthermore, no photoproduct can be detected by the UV/Vis spectroscopy of the solution, so the nature of the photoreaction remains elusive.

Conclusions

Compared to a solution DPDA/PEI LB-films show a significantly diminished intensity of the π-band in the UV/Vis spectrum, while the π'-band intensities is increased. The change in the intensity ratio is a consequence of the dense chromophore packing in the LB-film. Polarized irradiation causes an angle dependent increase in the absorbance in the π-band region, which previously has been interpreted to be due to a photoreorientation process. However, a decrease of the π'-band in the UV/Vis spectra and the C≡C vibration band in the grazing angle reflectance IR-spectra indicate a angle dependent excitation and subsequent photoreaction of the chromophores, which nature remains elusive. The angle dependent increase in absorbance in the π-band region is conjectured to be to partial reversal of the intensity ratio changes due to a less dense packing of intact chromophores. From experiments in which the irradiated LB-films have been dissolved, the amount of reacted chromophores can be estimated to be smaller than 20%.

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