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LB films of photochromic polyglutamates

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Summary

Copolymers bearing various contents of photochromic azobenzene chromophores and long alkyl chains covalently bound to a polyglutamate main chain have been synthesized. The chromophore can be isomerized to a high extent by irradiation with UV light. The copolymers can be spread on a LANGMUIR trough. The spreading behaviour is affected by the content of cis-isomer, which is adjustable by irradiation. The effects are more pronounced for the copolymer with higher content of chromophore. The use of the copolymers for optical data storage is considered.

Introduction

In the last few years there has been a great progress in the field of optical data storage. The systems used are polymeric liquid crystals /1-3/ or LANGMUIR-BLODGETT films /4, 5/. In these systems the photochromic azobenzene is the working unit, inducing disorder or reorientation due to the trans-cis isomerization /6, 7/.

To achieve high stability and homogenity in LB films a new type of surface active substances has to be developed. These requirements are met by polymers with a rigid backbone and flexible side chains, socalled "hairy rods" /8-11/. It is possible to incorporate oleophilic azodyes in the monolayers of these "hairy rods". The dye is dissolved in the liquid like side chain region /12/. These monolayers can be transfered and the resulting LB films can be used for optical data storage employing a special read out technique /4, 13/.

To enhance stability and sensitivity the dye has to be bound covalently to the polymer backbone preventing migration and crystallization of the dye. Therefore copolymers bearing azobenzene moieties and long alkyl chains as side groups of α-helical polyglutamates were synthesized.

We will report on the photochromic and spreading behaviour of these polyglutamates.

Synthesis

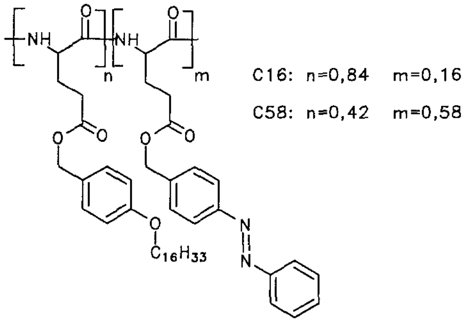
Poly(5(4-phenylazo)benzyl-L-glutamate-co-5(4-hexadecyloxy)benzyl-L-glutamate) was synthesized according to procedures described previously /14/ by mixing the appropriate amounts of the corresponding N-carboxyanhydride monomers, obtained according to literature procedures /14, 15/.

The composition of the copolymers was determined by means of UV-Vis spectroscopy using the extinction coefficient of the unipolymer /14/ to 16% (C16) and 58% (C58) azobenzene component.

The copolymers were characterized by means of ^{1}H-NMR, IR, GPC and DSC.

C58 has an estimated molecular weight of about $1.0 \cdot 10^5$ g/mol (GPC, by comparison with polyglutamates of known molecular weight). There are no transitions detectable by DSC in the temperature range between 293K and 500K.

The polymer with lower content of azobenzene groups (C16) has a molecular weight $M_n = 4.0 \cdot 10^4$ g/mol (membraneosmosis, THF, 310 K). This polymer exhibits a transition detectable by DSC at 312 K, which is related to the "melting" of the alkyl chains /15/.



Results and Discussion

UV-Vis Spectroscopy

In both copolymers the trans-azobenzene group can be isomerized to high extent into the more polar cis-azobenzene by means of UV irradiation.

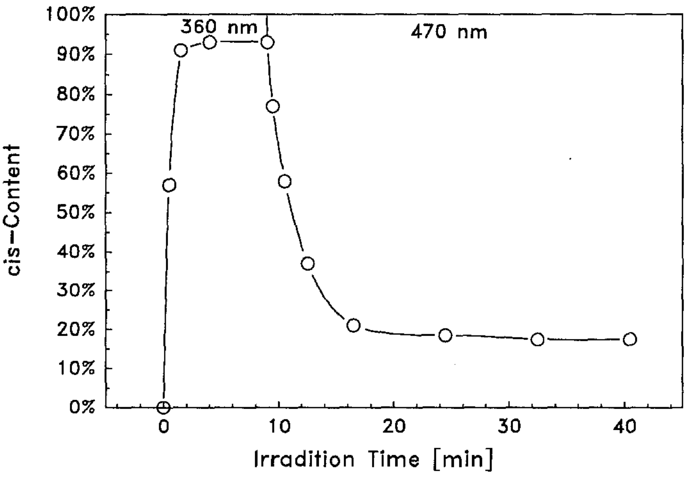


Fig. 1: Cis-content of a solution of C16 in $CHCl_3$ as function of the irradiation time and the irradiation wavelength

The cis-content in the photostationary state was determined to 93% for C16 (see fig. 1) and to 88% for C58. By means of irradiation with visible light the cis to trans isomerization can be achieved. The trans photostationary state contains 18% cis-isomer for C16 and 21% for C58.

The slightly lower extent of isomerization for C58 may be due to the higher concentration of chromophore along the backbone, resulting in aggregation to some extent which lowers the efficiency of the isomerization /16/.

Spreading Behaviour

C58

The isotherms obtained for C58 from dark adapted and irradiated solutions are shown in fig. 2. The surface area per monomeric unit A_0 is 0.322 nm^2 for the trans-state and 0,328nm^2 for the cis-rich state, respectively, which are the same within the experimental error.

There are plateaus at about 20-25 mN/m in the isotherms which can be ascribed to the formation of a bilayer /17, 18/. The surface pressure within the plateau is slightly higher for the irradiated sample (23 mN/m for the irradiated, 21 mN/m for the dark adapted), indicating stronger interaction of the more polar film with the water molecules at the interface.

When the temperature of the subphase is raised from 298 K to 318 K A_0 increased to a value of 0.343 nm^2 due to the thermal expansion. The surface pressure within the plateau decreases to 16 mN/m due to the higher mobility of the side chains.

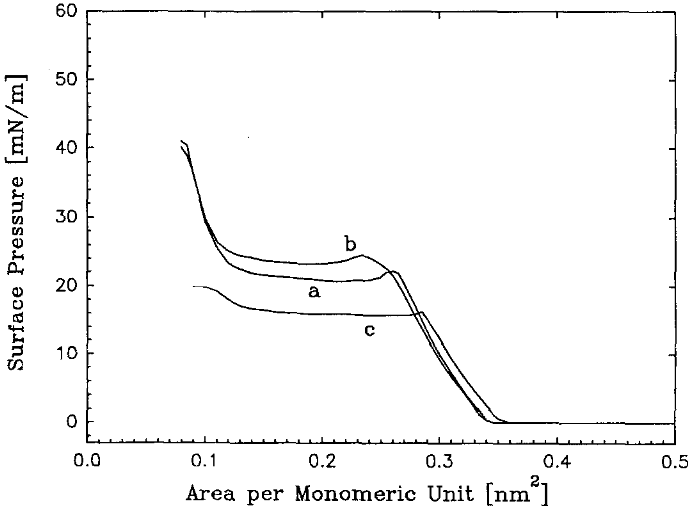


Fig. 2: π-A Isotherms for C58 a) dark adapted at 298 K, b) irradiated at 298 K, c) dark adapted at 318 K

C16

At low temperatures the isotherms of C16 show no plateau, but a point of inflexion. This

point is also related to the formation of bilayers /18/.
On increasing the temperature of the subphase the surface pressure for this transition decreases, concomitantly the point of inflexion broadens and changes into a plateau (see fig. 3). This temperature behaviour can be explained taking into account the "melting" of the alkyl chains (according to DSC measurements at 312 K). The greater mobility of the chains in the liquid like state allows the formation of bilayers at lower surface pressure.

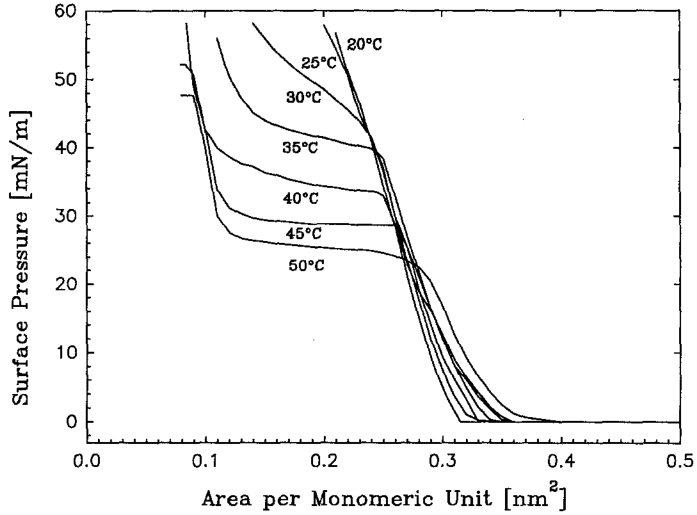


Fig. 3: π-A Isotherms at different temperatures for dark adapted C16

There are only small differences between monolayers obtained from dark adapted and irradiated solutions, respectively, both showing the temperature dependence described above. At lower temperatures the surface area is somewhat higher for the cis monolayer, above the "melting" point of the alkyl chains the difference disappeares (see fig. 4). The cis-azobenzene moieties are not as good compatible with the packing of the alkyl chains as the trans-isomer /19/, resulting in a higher area per residue. When the side chains are liquid like the disturbance due to the cis-azobenzene is not as pronounced as in the crystalline state.

Surface Plasmon Microscopy/20/

It is possible to transfer the monolayers onto substrates suited for surface plasmon microscopy. The LB films obtained are very homogeneous. Affords to use these films as information storage systems in an experimental setup described before /4/ failed. It was not possible to obtain a readable refraktive index pattern by irradiating the film.
This result was unexpected, because the differences in the spreading behaviour (larger area per monomeric unit for an irradiated sample) suggested that the trans-cis isomerization should induce some disorder in the LB film at the irradiated sites. The content of chromophore was high in comparison to the system used by other authors (only 7 mol% dissolved dye in the mixture /4/). But recently for a side chain LC polymer the

necessity of very high content of covalently bound chromophore was found /5/.
To enhance the content of covalently bound chromophore preserving the good spreading behaviour, unipolymers bearing azobenzene derivatives with alkyl chains have to be synthesized. Investigations in this field are under progress.

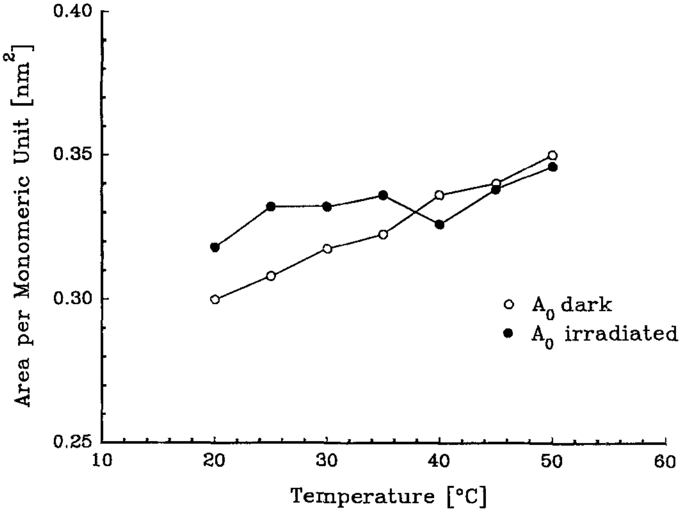


Fig. 4: Surface area per monomeric unit A_0 as function of subphase temperature for dark adapted and irradiated samples of C16

Experimental

^{1}H-NMR spectra were recorded with a Bruker WP 80 SY instrument. $CDCl_3$ was used as solvent though it is a helix forming solvent because the lack of solubility of the copolymers in helix breaking solvents like trifluoroacetic acid. Due to the α-helix conformation, signals arising from the backbone protons are to broad to be evaluated.
IR spectra were recorded on a Perkin Elmer 398 instrument as film cast from $CHCl_3$. The thermograms were obtained with a Perkin Elmer DSC 2a. UV spectra were recorded on a Perkin Elmer Lambda 5 instrument. The content of cis-isomer was determined using the method of FISCHER /21/.
Irradiations were carried out with a 125 W high pressure mercury lamp (Phillips HPK 125), employing a cut off filter to obtain light with a wavelength $\lambda > 470$ nm (DEMA FW-161) and a band pass filter for light with $\lambda = 360 \pm 50$ nm (DEMA UVW-55).
The copolymers were spread from $CHCl_3$. The concentrations were 0.3 - 0.5 g/l. The solutions were kept in the dark for at least one week to ensure full trans-configuration or were irradiated for at least 30 min for photostationary state. The solutions were handled under red light conditions. A Lauda FW 1 trough filled with "Milli-Q" water was used recording the surface pressure / surface area isotherms. The velocity of the barrier was 0.9 cm/min. A period of at least 20 min was between spreading and compression of the film. The area per monomeric unit A_0 was determined by extrapolating the linear portion of the isotherm to zero pressure.

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