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Photomechanical effects in Langmuir monolayers from polymers containing azobenzene groups

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The mechanical response of photoirradiated spread monolayers of a polymer containing azobenzene groups in the main chain was studied.

It is well known that polymers containing azo groups are photosensitive; *i.e.*, they may be isomerised by electromagnetic radiation.[1] Exposing a macromolecule of azobenzene to 420 nm light pulses drives it into its lengthened *trans* state, whereas 365 nm light pulses cause the molecule's backbone to contract while azo groups pass to the bis state. A photomechanical response produced by the *trans–cis* switching of adsorption and Langmuir monolayers of various azobenzene-containing compounds on the water–air interface has been reported.[2] Changes in the equilibrium and dynamic surface tension of water-soluble surfactants containing azobenzene upon illumination with UV light have been described.[3–5] The photomechanical response of the Langmuir monolayers of dendrimers bearing azobenzene groups was also described.[6] Polymeric photochromic compounds bearing azobenzene side chains can change the occupied area on the air–water interface submitted to the alternative UV and visible radiation.[7–9] X-ray diffraction data suggest that the monolayer became thicker for the *trans* form than that for the *cis* form, and the side chain should stretch to the direction perpendicular to the water surface with the conformational change from *cis* to *trans* form, in addition to the longer chain of the *trans* form.[10] Hugel *et al.*[11] found the deformation of azobenzene macromolecules exposed to light using AFM techniques and estimated the work produced by a single molecule during photoisomerisation cycles. This experiment was the first demonstration of an optomechanical machine consisting of a single macromolecule as a deformable body.

Here, we report our preliminary results on the photomechanical effect manifested by the Langmuir monolayers of a new polymer containing azobenzene groups in its backbone.

An amphiphilic copolyester with azobenzene groups located in the macromolecular backbone was synthesised by the acceptor-catalytic polycondensation[12] of terephthalic acid chloride with polyethylene glycol (molecular weight of 400), 4,4′-azophenol and 3,3′-dichloro-4,4′-dihydroxydiphenylpropane in dichloroethane in the presence of triethylamine (2 h, 40 °C) (Scheme 1). The photochromic copolymer with a molecular weight of about 15000 was obtained. This copolymer is readily soluble in methylene chloride and other organic solvents.

Monomolecular films of this azobenzene-containing copolymer were prepared by the Langmuir technique at room temperature. Water for the subphase in the Langmuir trough was distilled and passed through a Milli-Q water purification system (surface tension of 72.5 mN m^{-1} at 20 °C). Methylene chloride (Aldrich, A.C.S. spectrophotometric grade) was used to prepare polymer solutions. The copolymer was spread from ~1 mg cm^{-3} methylene chloride solutions onto an aqueous subphase. The equilibration time for surface monolayers before compression was 10 min. The surface pressure–area (π–A) isotherms were obtained for nonilluminated Langmuir monolayers. The films were compressed up to the desired surface area A and afterwards the kinetic relaxation curves $\pi(t)$ were recorded by maintaining this area constant (Figure 1). The parameters of the relaxation curves were found and controlled as described elsewhere.[13] After a relaxation time, the Langmuir monolayers were illuminated using an ultraviolet lamp (100 W) equipped with a 365 nm filter from a distance of 40 cm starting at the point t_1 in time. Immediately, a considerable decrease in the surface pressure π was observed testifying for isomerisation processes in the monolayer. Switching off illumination at the time t_2 led to the imminent stopping in the decrease of π, which remained constant during the time of darkness. Illumination of the monolayer with visible light (440 nm) starting at the point t_3 in time produced a small increase in the surface pressure, which also stopped to grow in the darkness at the time t_4.

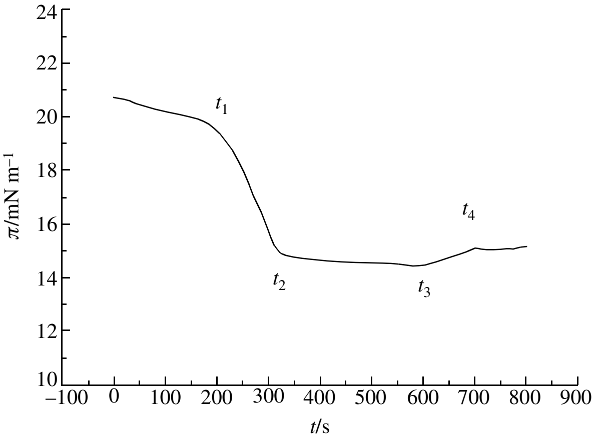
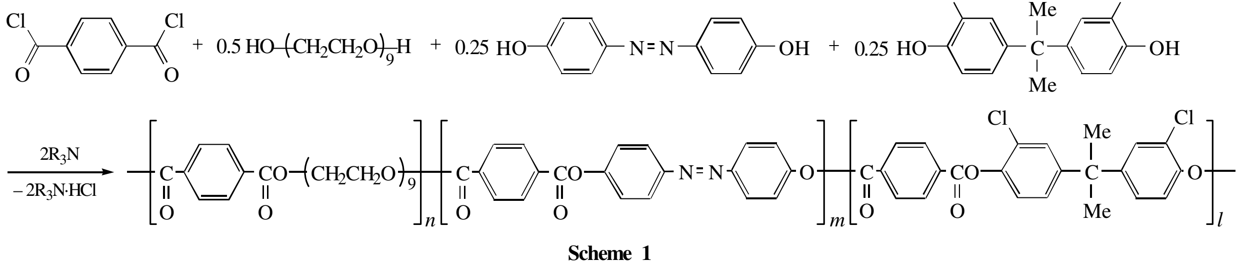


Figure 1 Photoinduced variation of surface pressure π *vs.* time t for a Langmuir monolayer of the polymer containing azobenzene groups in the main chain.

The observed irreversibility of the photoinduced deformability of monolayers of the copolymer containing azobenzene groups in the macromolecular backbone was unexpected. For example,



Scheme 1

Sidorenko *et al.*[6] reported the perfect reversible photoinduced deformation of azobenzene-containing dendrimers with an optimal structure as a response to multiply swithching the illumination lamp on. The Langmuir–Blodgett monolayers of polymers bearing azobenzene side chains deposited on a solid substrate also demonstrated, under certain conditions, a reversible photoresponsive behaviour.[14] Depending on the structure of these polymers, the Langmuir monolayers manifest[7] or do not manifest[14] the reversibility of photoinduced deformation.

In our opinion, the absence of reversibility from our copolymer may be due to a high content of polyethylene oxide moieties (~50 mol%), which govern the adsorption and the conformation of the macromolecule at the air–water surface. It has been reported,[13,15] that the spread monolayers of compounds with long oxyethylene (OE) chains manifest hysteresis in compression–decompression cycles because of the particular interaction of these long OE chains with water and their irreversible adsorption at the water surface. It seems that, after contraction of azobenzene groups to their *cis* forms inside a macromolecule under UV illumination, its size decreases to decrease the surface pressure. However, the switching of azobenzene groups to their stretched-out *trans* forms cannot increase the surface pressure by returning the conformation of the macromolecule to its initial extended state.

The optomechanical effect manifested by the Langmuir monolayers of the copolymer containing azobenzene groups can be used to move a load as the monolayer is compressed under UV illumination. Taking into account that the decrease of the surface pressure $\Delta\pi$ during a contraction cycle is about 5 mN m^{-1} for the initial surface pressure $\pi \sim 20$ mN m^{-1} and the elasticity module $E = d\pi/d\ln A$ of the monolayers is about 10 mN m^{-1} for the area $A \sim 100$ cm^2, the possible mean work, which may be delivered by the monolayer, is $W \sim \pi\Delta\pi/EA \sim 10^{-3}$ J. The mean area a_1 occupied by a macromolecule in the monolayer was estimated at $a_1 \sim 5$ nm^2; the delivered work per macromolecule is equal to $w_1 \sim WA/a_1 \sim 5{\times}10^{-19}$ $J \cong 10^2$ kT.

We believe that the reversibility of the photoinduced deformability of Langmuir monolayers of the copolymer containing azobenzene groups can be used for designing a photocapillary machine to transform light energy to mechanical work.

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