

Microscopic theory of photoinduced deformation of side-chain LC azobenzene polymers

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In recent years, photoresponsive liquid-crystalline (LC) polymers bearing azobenzene moieties in their side chains have been a subject of extensive investigations.^[1-3] These polymers have unique physical properties and fascinating potential in technical applications as smart materials. Upon photoirradiation, azobenzene moieties undergo trans-cis isomerization. As a result, a polymer changes its shape with respect to the polarization vector of the light.^[1] This effect is visible in such phenomena as inscription of surface relief gratings onto uncross-linked thin azobenzene polymer films^[1] and photoinduced bending of cross-linked azobenzene elastomers.^[2] These properties open up possibilities to use azobenzene polymers as data storage media, as mechanically tunable optical elements, as artificial muscles and actuators.^[2]

A number of models have been proposed to explain the origin of the photoinduced force. However, none of them provides a value of the photoinduced mechanical stress which would be enough to irreversibly deform glassy azobenzene polymers, i.e. larger than the yield stress typical for the glassy polymers (10-100 MPa). Moreover, none of the previous theories describes the effect of chemical architecture of azobenzene macromolecules on the photomechanical behaviour.

Here, we present a microscopic theory which is based on the assumption that photo-induced stress is caused by the reorientation of azobenzene chromophores affected by the light. We use an orientation potential of chromophores with respect to the polarization vector of the light introduced originally in ref. 3. Interaction of chromophores with the light results in the reorientation of polymer chains due to covalent bonding of the chromophores to the backbones. This leads to the appearance of mechanical stress. Minimizing the free energy, we determine the photo-induced stress as a function of the light intensity, temperature and orientational distribution of chromophores inside the macromolecules. We find that a sample can be either stretched or uniaxially compressed along the polarization direction depending on the polymer architecture in agreement with experiment.^[1] Further, we calculate the light-induced stress which turns out to be higher than the value of the yield stress expected for polymers. This allows us to explain the light-induced deformation of the azobenzene polymers even in the glassy state.

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