Light-Driven Surface Patterning of Supramolecular Polymers with Extremely Low Concentration of Photoactive Molecules

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ABSTRACT: Light-induced surface patterning in azobenzene-containing polymers and other materials is a widely studied phenomenon with possible applications in fields ranging from photonics to biology. Yet, the fundamental understanding of this purely photodriven mass transport remains inadequate, and existing literature fails to define a threshold chromophore content for mass transport to occur, if such a limit exists. This letter presents a systematic study of the relationship between chromophore concentration and mass transport using hydrogen-bonded polymer—azobenzene complexes, in which the chromophore concentration can be freely adjusted while keeping the polymer backbone unchanged. Essentially, we demonstrate that effective surface patterning can be induced even at an extremely low chromophore content of 1 mol %, when only every tenth polymer chain carries a single azobenzene molecular motor. Importantly, the results highlight the extraordinary photomechanical power of azobenzene and contribute to the fundamental understanding of the light-induced motions.
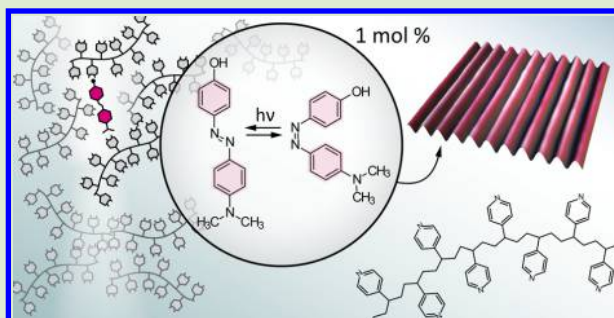
Interest toward light-responsive azobenzene-containing materials has increased tremendously in the past decade, with a continuous flow of literature reporting new photo-induced effects both at molecular and macroscopic level and from fundamental and applied point of view.[1,2] The intriguing properties of azobenzene-containing systems, which nowadays come in a wide variety of materials from biological matter to liquid crystals, are brought about by the reversible and efficient *trans—cis* photoisomerization of azobenzene.[3−5] This molecular-level structural change can initiate motion on much larger length scale, even macroscopically.[6−8] One of the most widely studied phenomena is the photoinduced surface patterning. Illuminating a thin film of azobenzene-containing material, typically polymer, with a light interference pattern induces macroscopic movement of the material that results in the formation of a temporally stable topography grating of up to hundreds of nanometers on the film surface.[9,10] In typical experiments, the surface pattern has a sinusoidal profile, often referred to as a surface-relief grating (SRG). However, the mass transport is dictated by the spatial intensity and polarization variation of the incident light, and arbitrary structures can be inscribed as well.[11,12] This simple and reversible process only requires a single fabrication step to inscribe high-quality patterns, which makes it attractive for a number of potential applications in photonics and nanotechnology and for organizing other material systems.[13−16] The grating formation has been studied in various azobenzene-containing systems, and besides traditional covalent synthesis, supramolecular function-

alization has been established as a powerful tool to design photoresponsive polymers that undergo efficient light-induced mass transport.[17−20]

The mass transport process in azopolymers is a highly complicated cascade of events that originates from molecular-scale photoisomerization. The driving mechanism depends both on the experimental parameters and the material itself, and a universal theory is still under debate.[21−23] Furthermore, a thorough understanding on how the polymer structure affects the surface patterning efficiency has not been reached. Known important parameters include molecular weight and the glass transition temperature of the polymer,[24,25] as well as the azobenzene content of the material.[26−29] The effect of chromophore concentration is particularly interesting as it can help to gain fundamental understanding on how much power the azobenzene isomerization reaction can actually translate into large macroscopic movements. The concentration dependence of mass transport efficiency has been studied in many systems with intermediate or high azobenzene concentrations. Andruzzi et al.[27] and Börger et al.[26] reported an optimum degree of functionalization on the order of 75 mol %, above which the efficiency of SRG formation decreases due to intermolecular interactions between adjacent chromophores. Moreover, Fukuda et al.[28] reported an exponential increase of

the surface modulation depth as a function of dye content up to 50 wt %, after which the depth remained constant. In the course of our own studies with supramolecular systems, this relationship has been observed to be very material-specific, and both nonlinear and linear behavior has been reported.[29−31] To the best of our knowledge, none of the existing theories takes into account the effect of azobenzene content on the surface-patterning mechanism nor gives suggestions on the lower limit of azobenzene content that is still capable of inducing mass transport. Moreover, literature does not provide any previous experimental data on the effect of azo content on SRG formation below molar fraction of 5%, even if this data might influence the understanding of the driving force behind light-induced mass transport. It seems that the common interest around surface-patterning phenomenon has been to develop ever more efficient materials, in which medium-to-high functionalization levels are beneficial. Also, it is very time-consuming and tedious to prepare a series of polymers with varying chromophore content with the tools of covalent synthesis. However, with the help of supramolecular assembly, the azo content of a system can be altered easily. The noncooperative nature of hydrogen bonding in particular enables one to systematically study the effect of chromophore concentration on the optical properties of a material system, as even equimolar dye−polymer complexes can be fabricated without excessive aggregation or phase separation.[32] In this Letter, we demonstrate light-driven mass transport in hydrogen-bonded glassy materials with extremely low azobenzene content. The results provide new implications into the limits of the mass transport phenomenon as surface patterns can be inscribed even when majority of polymer chains bear no photoresponsive azobenzene units at all.

We study hydrogen-bonded complexes of poly(4-vinyl-pyridine) (P4VP) and 4-hydroxy-4′-dimethylamino-azobenzene (OH-DMA), which have previously proven to be efficient materials for inscribing SRGs.[33] In contrast to our previous studies, where the aim has been to show that the optical properties of hydrogen-bonded complexes can be matched to those of their covalent equivalents, we now systematically decrease the amount of azo in the system in order to find a critical concentration limit, below which mass transport no longer occurs. The chemical structure of the nominally stoichiometric complex (100 mol % functionalization) is shown in Figure 1a. A series of complexes with chromophore
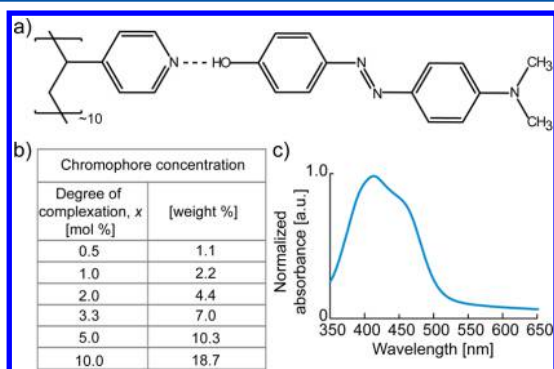
concentration from 0.5 up to 10 mol % were prepared by simply mixing of solutions containing the chromophores and the polymer. The respective chromophore concentrations as weight percentage are listed in Figure 1b, and the UV−vis spectrum of the 10 mol % complex is shown in Figure 1c. Note that the lower limit of 0.5 mol % corresponds to the case where every 200th polymer repeat unit is occupied by the azobenzene. P4VP with very low molecular weight (∼1000 g/mol), having approximately 10 repeat units, was chosen for the study to obtain fast dynamics in surface patterning.[33] Hydrogen bonding between the constituents has been confirmed by infrared spectroscopy in the course of previous studies on the same complex.[34] Sample films with thicknesses above 2.5 μm were prepared by drop-casting the complex solutions on glass substrates and confirmed to be amorphous by polarized optical microscopy. The photoinduced surface-patterning experiments were performed on the sample films using circularly polarized light with wavelength of 488 nm and intensity of ∼200 mW/cm^2 in a Lloyd's mirror setup.[10] The inscription time was fixed to 10 min in order to compare the efficiency of SRG inscription within the concentration series. Formation of the surface structure was monitored in situ by measuring diffraction from a low-power red laser beam through the illuminated area, and the diffraction efficiencies were further confirmed by comparing the power of the probe beam through an unilluminated area to that of the diffracted beam.

The evolution of the diffraction efficiency during the SRG inscription is shown in Figure 2a, and the values of diffraction efficiency after 10 min are shown in Figure 2b. The inscription data expectedly shows that the efficiency of mass transport is strongly dependent on the chromophore concentration, becoming significantly more efficient when the concentration is increased. The surface modulation depths of the SRGs were
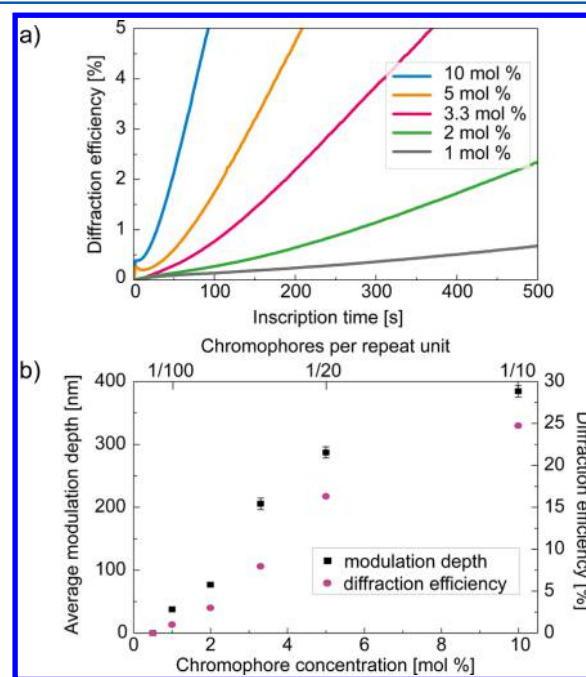

Figure 1. (a) Chemical structure of the nominally stoichiometric complex between P4VP and OH-DMA, (b) the chromophore concentration as weight percentage in the studied complexes, and (c) the normalized UV−vis absorption spectrum of a 10-mol % film.

Figure 2. (a) Evolution of diffraction efficiency as a function of inscription time, and (b) average modulation depths (black cubes) and the diffraction efficiencies (violet circles) of the SRGs as a function of chromophore content. The error bars present the standard deviation in the AFM data.
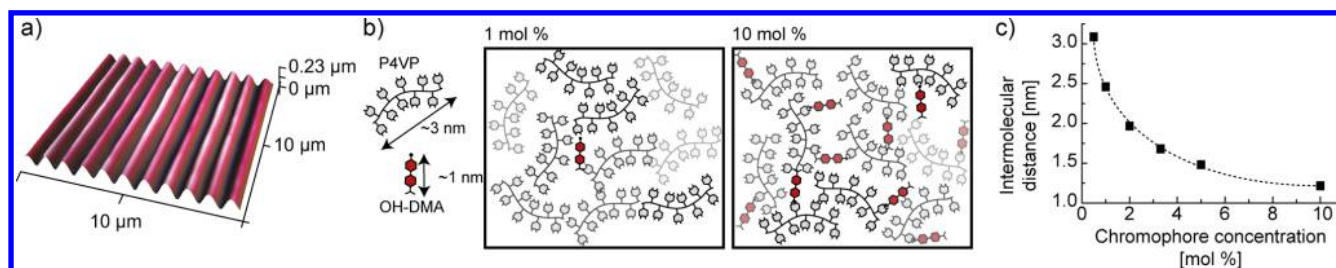
Figure 3. (a) 3D AFM height image of an SRG in the drop-cast 1 mol % sample after 90 min inscription, (b) visual representation of the 1 and 10 mol % complexes, and (c) the average distance between the chromophores as a function of chromophore content.

obtained by atomic force microscopy, and the average values are presented in Figure 2b as a function of chromophore molar percentage and chromophores per polymer repeat unit (second *x*-axis). A direct correlation to the diffraction data is observed, as the SRG modulation depth grows steadily when the chromophore concentration is increased. In this context the most interesting part of the data, that is, the very low chromophore concentrations, shows that the light-induced mass transport takes place even at remarkably low azobenzene concentration: the sample with only 1 mol % OH-DMA yielded a 40 nm SRG within 10 min of inscription. On the other hand, no grating was formed on the 0.5 mol % complex even within a 30 min inscription period. We can thus conclude that the upper limit for the onset concentration of mass transport is 1 mol % in the current material system. Upon prolonged irradiation (90 min, 250 mW/cm^2), the 1 mol % sample yielded a considerable modulation depth of 170 nm (see Figure 3a) with no sign of saturation in the diffracted signal. Hence, it is likely that by further increasing the irradiation time or intensity, an SRG with modulation depth of hundreds of nm can be inscribed even in samples bearing negligible amount of azobenzenes. Furthermore, as the film thickness is known to have an effect on the efficiency of SRG inscription,[35,36] it is interesting to see whether the potential substrate effects would affect the onset concentration. Hence we prepared a 100 nm thin sample film of the 1 mol % complex by spin coating, followed by SRG inscription. In this case, the irradiation time was set to 30 min because SRG formation is significantly slower in very thin films compared to the drop-cast samples. This experiment resulted in an SRG of 10 nm, indicating that the amount of azobenzene needed to induce mass transport is not affected by film thickness.

It is rather astonishing that SRGs can be inscribed in complexes containing only 1 mol % of azobenzenes, regardless of the film thickness. Such a complex contains nominally one azobenzene molecule per 100 polymer repeat units, and given that each polymer chain carries about 10 repeat units, an azobenzene unit is attached only to every tenth polymer chain, while the other nine remain azobenzene-free. Despite this, the material is capable of light-induced mass transport to produce a grating with modulation height 2 orders of magnitude larger than the size of an individual complex. It is also noteworthy that when the azo content is increased 10-fold, one azobenzene molecule occupying one polymer chain, the SRG modulation height is already almost 400 nm after 10 min inscription. The 1 and 10 mol % complexes are schematically represented in Figure 3b to visually demonstrate the relative amount of azobenzene responsive for moving the photopassive polymer chains.

In order to rationalize the light-induced mass transport at such low azobenzene content, it is possible to theoretically estimate the average intermolecular distances between the chromophores to see whether intermolecular interactions play a role in the process. Taking the inverse value of the number density of the chromophores N, we get the volume occupied by a single chromophore. Now the cubic root of this value gives an estimate for the average distance between the chromophores r, as

$$r = \sqrt[3]{\frac{1}{N}} = \sqrt[3]{\frac{M}{w_i \rho N_A}}$$

where w_i is the chromophore weight fraction, ρ is the density of the material, N_A is the Avogadro's number, and M is the molar mass of the chromophore. The density of the material is estimated to be 1.2 g/cm^3, which is slightly more than for pure P4VP. The calculated average intermolecular distances between the OH-DMA molecules as a function of degree of complexation are presented in Figure 3c. For the 1 mol % complex, the approximated intermolecular distance is far larger than intermolecular distance reported for the azobenzene self-assembled monolayers that suffered from excitonic coupling quenching the photoisomerization.[37,38] Taking into account the proposed r^{-3} distance dependence for excitonic coupling,[39] we can clearly state that azobenzene photoisomerization at 1 mol % is not affected by neighboring azobenzenes, but the grating formation is caused by the action of dispersed, independent azobenzene units in a polymer.

We believe this finding to be pertinent in view of understanding the limits of photoinduced mass transport in amorphous azopolymers, and call for modeling efforts to profoundly explain the SRG formation at extremely low azobenzene concentrations. We would particularly like to highlight the theoretical work of Saphiannikova and co-workers[23,40] stating that the orientational redistribution of azobenzene chromophores upon irradiation with polarized light brings about directional mechanical stress that is responsible for the photoinduced surface deformation. However, for the stress to be larger than the yield stress of the material, a relatively large chromophore number density (each oligomer chain contained 20 chromophores;[23] cf. herein only every tenth chain is photoactive) was assumed. Recent experimental findings on "photoinduced fluidization"[41−44] and especially the observation that photoinduced mechanical changes of thin azopolymer films may be greater in phenol-pyridine hydrogen-bonded polymer-azobenzene complexes as compared to covalently functionalized side-chain azopolymers[45] should be thoroughly understood in order to gain insight into the complicated photo-mechanical response of azopolymer thin films and its fundamental limits. If the photoinduced plasticization is taken into account together with the photoinduced directional stress proposed by Saphiannikova et al., one can assume that above a

certain threshold concentration the net effect of these two photoinduced forces overcomes the yield stress of the polymer. Finally, due to the dynamic nature of hydrogen bonds, it may be possible that the chromophores are able to hop between polymer chains, and hence interact with several chains during the mass transport process. This could in part explain why in the present materials SRG formation still occurs at very low azo content.

In conclusion, we have performed a systematic study on the effect of chromophore concentration on photoinduced mass transport in polymer–azobenzene complexes. The supramolecular assembly enabled us to demonstrate that effective mass transport can be induced even at extremely low chromophore content. Furthermore, in both thick (>2.5 μm) and thin (100 nm) sample films the smallest studied amount of azobenzene needed for SRG formation was 1 mol %, indicating that the thickness only affects the efficiency of light-induced mass transport. Amazingly, a surface-relief grating of 170 nm could be induced in a thick film which has, on average, only one azobenzene molecule per every hundred polymer repeat units, that is, 90% of the polymer (oligomer) chains are in fact photopassive. These results point out that not every polymer chain has to carry a photochromic unit for the mass transport to be induced. The fact that a very small weight fraction of azobenzene is needed for surface patterning can be beneficial for applications, where the strong absorption of the chromophores is a problem. Moreover, it has been demonstrated that the chromophores can be selectively removed from the system altogether after SRG inscription, but not without decreasing the height of the inscribed pattern.[18] Using a material with very low chromophore content, decrease in the modulation depth should be negligible. Even if the critical azo concentration presented here is highly specific to the current material system, the results definitely provoke interest in performing a more systematic study involving different chromophores and binding motifs and theoretical modeling to be performed in the future, allowed by the facile noncovalent functionalization strategy.

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Notes
The authors declare no competing financial interest.

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