Cooperative interaction in azopolymers upon irradiation

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We present two optical experiments which permits to evaluate individual and collective behaviours of molecules leading to a well-organized pattern in a randomly activated molecular assembly; in a first experiment a white light and a laser beam are sent together; in a second experiment a low-power coherent beam carrying polarization and wavelength information is used to organize a surface relief grating on a photochromic polymer thin film which is photo-activated by a powerful incoherent beam; we show that collective movements originate at the molecular level.

Azobenzene is the basic molecule for a wide range of applications, from dye indicators and nonlinear optical chromophores, to quantum interferences.[1] The molecule exists in two geometric isomers *trans* and *cis*. One of the important properties of these chromophores results from the photochemical *trans–cis* isomerization induced by UV or visible light.[2] In these molecules, photoisomerization induces conformational changes in the polymer chains, which in turn leads to macroscopic variations of the properties. Another effect related to the photo-initiated process is molecular reorientation into directions perpendicular to that of the light polarization.[3] When azobenzenes are bound to or doped into a polymer matrix, the constant and rapid *trans–cis* photoisomerization activity results in an efficient molecular motion. This molecular motion gives rise to coordinated motion.[4,5] Irradiation of thin azopolymer films with an interference pattern of coherent light can induce massive movements of the polymer material over long distances and a controlled modification of the film surface that results in a micrometer-deep surface relief grating (SRG).[6] More recently, SRGs have been produced in a one-step irradiation process in standard laboratory conditions with a controlled laser beam polarization.[7,8] Practically, one single beam with controlled polarization can photo-induce a SRG whose wave-vector direction is parallel to the light polarization. Multistate addressing by polarization could be achieved in this way. The driving force responsible for SRG formation is a random molecule migration almost parallel to the polarization direction. Self-organisation is initiated by noisy random fluctuations of the molecular positions. The local perturbations are enhanced by interference of the scattered light waves, thus forming regular patterns. Light initiated spontaneous pattern formation arises from the interplay between self-action (*e.g.* photoisomerization) and long range interaction (*e.g.* diffraction). The final state is self-organized as a coherent grating. In those experiments of self-induced SRG formation the photoactive molecules were excited by a coherent beam. We have also previously shown that a well-defined SRG can be induced in an azopolymer thin film by the combination of a low power coherent laser beam with another high power incoherent and unpolarized beam.[9] The low power beam carries coherent information about the pitch and orientation of the diffraction grating and the high power beam activates the molecules to permit the movement and the structure. Molecules exchange position information through scattered light showing this is the process by which self-organization takes place. We seek in this work for the individual *vs.* collective behaviour of molecules during self-organization. We present two sets of experiments that permit to study the individual and collective behaviours of molecules submitted to coherent and incoherent light excitations.

In the first experiment the molecules are alternately illuminated by a coherent beam from a laser and by a solar-like white light from a xenon-arc lamp (Fig. 1(a)). They will have the choice between two alternatives: to cooperate to the construction of a SRG under the coherent light, or to create a random pattern on the polymer surface under the

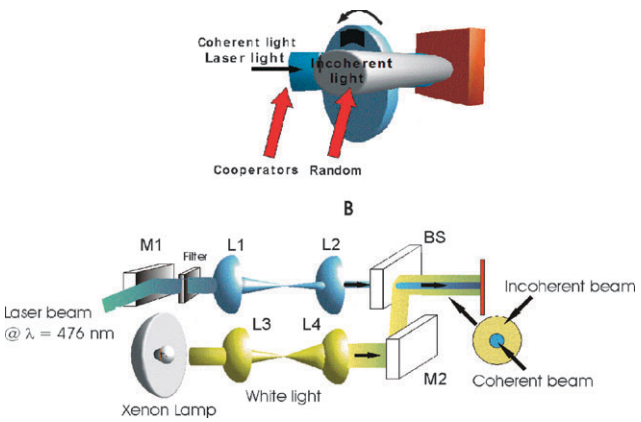

Fig. 1 Scheme of the experimental set-up.

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incoherent light beam.[9] The coherent beam carries information about the SRGs through its polarization, incidence and wavelength, corresponding to the so-called stimulated Wood anomaly condition.[10] An incoherent light beam allows a random molecular motion. If molecules can either move randomly without correlation or can be self-organized in a coherent grating, they have the choice between the two alternatives. The paradigm is about the way cooperative behaviour takes place among 'self-interested' individual molecules or, in other words, how robust is cooperation in the presence of disorder? We thus get a measurement of cooperativity with the efficiency or speed at which a coherent pattern is formed. We aim at showing how without any central control, individual molecules respond to simple local informations in ways that allow the whole system to create a pattern resulting from interactions between molecules.

In the second experiment (Fig. 1(b)), we experiment on a sort of 'cognitive' process or acquisition of information. A large power incoherent beam assists a low power coherent beam to create self-organization into a SRG.[11] Information is carried by the signal beam and consists in the orientation and pitch of the grating. Information on the SRG pattern is retrieved as the diffraction characteristics of the coherent signal beam.

Samples are polymer films made from a highly photoactive azobenzene derivative containing heterocyclic sulfonamide moieties[12] (Fig. 2). 1 μm-thick films were deposited on glass substrates by spin-coating of the polymer from a 50 mg ml^{-1} solution in THF. The $\lambda = 476.5$ nm laser line of a continuous argon ion laser was used as a coherent beam to excite the azo-polymer close to its absorption maximum which peaks at 438 nm. Absorbance at the working wavelength is 1.6 and the $T_g = 339$ K. The molecular mass of the polymer determined by GPC was between 14 000 and 19 000. The set-up for the first experiment is shown in Fig. 1(a). The white light beam has a power density of 0.4 W cm^{-2}. Both the laser beam and the incoherent light are sent through a wheel with a half-circle slot with 10 cm diameter and 10 mm width. The slot allows sending alternately the coherent laser beam and the white light at a frequency of 0.5 Hz. Alternation between the coherent or signal beam and the incoherent beam is chosen not only to limit thermal effects but also to allow the molecular system to relax in between illumination steps. The frequency of 0.5 Hz is the time scale at which the molecular movements take place in the polymer. For both beams the diameter of the collimated light impinging on the polymer sample is fixed to 5 mm with a combination of lenses. Both beams overlap on the sample which is set perpendicular to the incident laser beam. The sample is exposed to the light for about 1 h, corresponding approximately to the first-order diffracted beam intensity reaching a maximum. The laser beam power is adjusted by neutral density filters.

In the second two-beam experiment, we probe the time evolution of the diffraction intensity when the polarization of one of the incident beams is rotated. The experimental set-up is sketched in Fig. 1(b). The photoinduced self-organization experiment is conducted with the superposition of a very weak laser beam and a high power white lamp (Fig. 1(b)). The $\lambda = 476.5$ nm laser line is used to excite the azopolymer. It acts as the signal beam (0.35 W cm^{-2}) which carries the information on the SRG. The incoherent white light beam from the CW xenon-arc lamp passes through a hole and is shaped by an afocal before superposition on top of the signal beam. The beam diameter of the white light is 5.8 mm, larger than the 2.1 mm-diameter 0.07 W cm^{-2}-intensity laser beam. A piece of glass is inserted in the common path of the two beams to prevent UV irradiation from the white light that could damage the sample. The thinner signal beam is at the center of the 0.35 W cm^{-2} intensity pump beam (Fig. 1(b)) and its polarization is linear and vertical. In all the experiments we have controlled that no thermal effects are induced and that the laser beam power does not damage the sample.

We define in broad outline as 'cooperators' the molecules illuminated by the coherent laser beam in contrast to the molecules illuminated by the incoherent white light (see Fig. 1(a)). Fig. 3 shows the power spectral densities (the Fourier transform which is also the scattered intensity pattern) of the surface grating relief induced using different coherent laser beam powers (first experiment).

The maximum laser beam power is fixed to 0.6 W cm^{-2}. Measurements were made corresponding to 2.8, 8.8, 13, 57 and

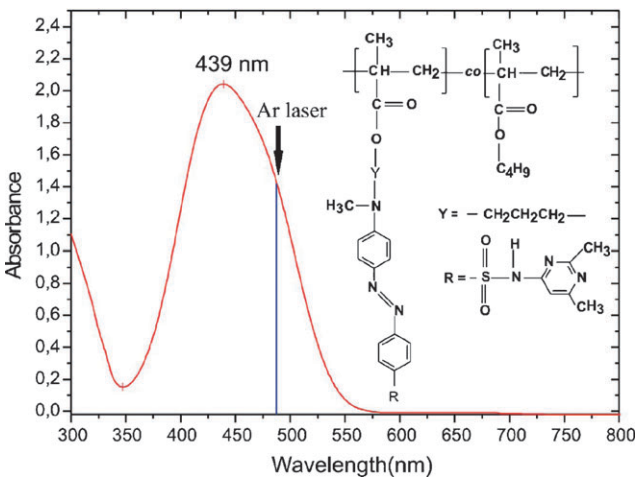

Fig. 2 Absorption spectrum and structural formula of the azopolymer thin film.

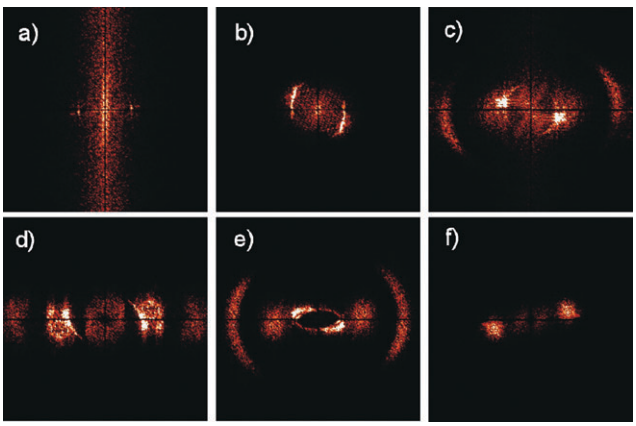

Fig. 3 Power spectral densities (PSD) for a ratio between cooperators and random movement of molecules of (a) 2.8%, (b) 8.8%, (c) 13%, (d) 57%, (e) 100%, and (f) without incoherent light.

100% of the signal laser beam power sent onto the sample. A regular pattern characterizes coherent self-organization of the surface. The corresponding power spectral density is given as a reference in Fig. 3(f) obtained using 100% signal beam power. The two spots in that case correspond to diffraction in the first order of the SRG. Cooperative organization is visible with the two-spot pattern in Fig. 3(c) for a laser power of 13%. The two-spot pattern is accompanied by larger spectral frequencies that are clearly visible in the spatial Fourier transform. The grating depths for the different signal beam powers were extracted from atomic force microscopy (AFM) of the illuminated surface. Grating depths of 3, 5, 13, 35, 60 and 100 nm were obtained for the 2.8, 8.8, 13, 57 and 100% laser powers, respectively (Fig. 4) with a constant pitch of $\approx 0.8 \pm 0.1$ μm for Fig. 3(d)–(f). The depth increases in two steps with a threshold at 13% signal beam intensity. Fig. 3(c) and (d) show changes in the cooperativity process. In Fig. 3(c) the choice is still not well defined and a periodic grating is not fully constructed; additional spatial frequencies are present. In Fig. 3(d), the spectral component of the coherent grating is clearly visible. Thus transition in the cooperativity of the molecular organization takes place between 13 and 20% of the maximum laser intensity.

The effect of collaboration at larger signal powers appears as a transition in the self-organization process.

A proof of spontaneous SRG organization is given by appearance of a first order diffraction of the laser beam. Diffraction intensity provides information about the time evolution of the surface pattern. In the second experiment, the signal beam polarization was rotated after 1 h of interactions within the sample. Diffraction which follows the signal beam polarization then changes direction (Fig. 5). The behaviour is exactly the same as when the laser was used with a diffuser as an incoherent beam.[11] When the pump polarization is rotated instead of the signal one, after 1 h of interaction (stars in Fig. 5), diffraction continues to increase steadily after a 10 min time lag. This shows that a control on molecular organization is acquired by the low power coherent signal zbeam over the strong incoherent beam, whatever its polarization direction. The pump beam permits SRG growth but it does not contribute to the final state of the grating pitch and orientation. The time lag after pump polarization rotation

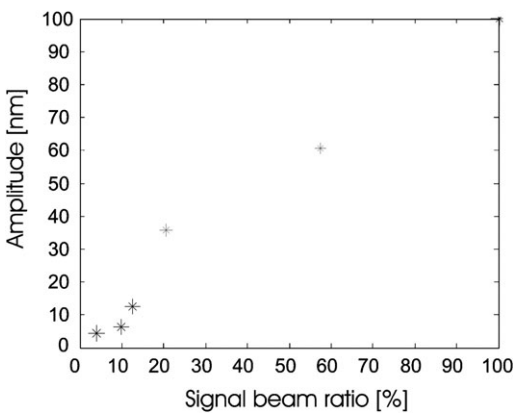

Fig. 4 SRG amplitude as a function of the ratio between coherent and incoherent excitation light sent to the sample.

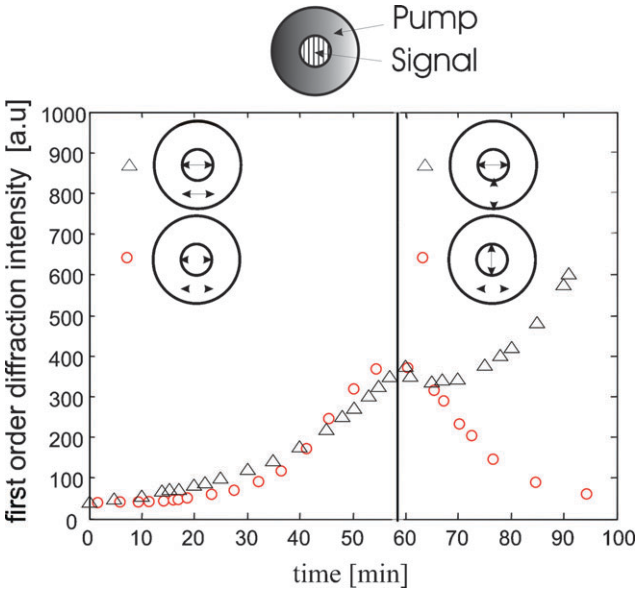

Fig. 5 First-order self-diffraction intensity as a function of time for a coherent beam as signal and an incoherent beam as pump. When the signal beam is rotated, the SRG changes direction and diffraction which is emitted in a perpendicular direction is no longer recorded by the photodiode (circles). When the pump beam polarization is rotated, the SRG continues to grow (triangles).

corresponds to the time needed for the restoration of a control. Practically it corresponds to the time taken by the molecules moving under the incoherent pump action, outside of the signal region, to receive the information on the grating characteristics from the signal beam. This time lag may be considered as the minimum acquisition time in the studied 'cognitive' process. This experiment provides further information on the control process within the azo-polymer film: a cooperative behaviour on the grating characteristics is driven by a few molecules differing in behaviour from the majority which undergo random molecular migration under the incoherent light exposure.

In conclusion, we have presented two experiments showing how collective final patterns are formed at the molecular level. We use the property of azobenzene chromophores to move by photoisomerization under the action of resonant light. The light sent onto the sample to switch the molecules can either be coherent or incoherent. If the light is coherent, then coherence is transferred to the system and a well defined SRG extends onto the whole surface under illumination. Information that is transferred to the azopolymer thin film surface manifests as a coherent grating pattern. In the case of an illumination with incoherent light, the locally coherent motions of the molecules cannot extend to the whole surface illuminated by the incoherent light and the molecules create a random pattern at the surface. In the first experiment, we alternated coherent and incoherent light on the azopolymer thin film. We have evaluated the condition for induction of a cooperative organization of the molecules. The result is the patterning of a SRG. The efficiency strongly depends on the coherent beam intensity sent and a transition occurs from disorder to collective organization. In the second experiment, where we sent simultaneously a tiny coherent laser beam with a large

power incoherent one, we evaluated the control taken by a small number of molecules 'informed' by information provided by the coherent beam to create self-organization over the large population of moving molecules.

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