LASER CONTROLLED MECHANICAL ACTUATION OF PHOTOCHROMIC-POLYMER MICROSYSTEMS

A. Athanassiou[1], M. Kalyva[1,2], K. Lakiotaki[1,3], S.Georgiou[1] and C. Fotakis[1,2]

[1]Foundation for Research and Technology-Hellas (FORTH), Institute of Electronic Structure and Laser (IESL),
P.O. Box 1527, 711 10 Heraklion, Crete, Greece
[2]University of Crete, Physics Department, Heraklion, Crete, Greece
[3]University of Crete, Chemistry Department, Heraklion, Crete, Greece

Abstract. The technology of micro/nanomechanical systems has brought the devices down to a scale where optical manipulation can become essential for their fine control. For that reason, a novel microsystem that undergoes mechanical actuation induced exclusively by photons is presented. This system is a polymer substrate doped with spiropyran photochromic molecules. It undergoes mechanical cycles after irradiation with ns laser pulses of low energy and specific wavelengths. The photoinduced mechanical movement is connected with the inter-conversion of the spiropyran molecules between different isomeric forms, upon irradiation at appropriate laser wavelengths. These photochromic inter-conversions were found to activate the polymer matrix, resulting in its contraction and lengthening in a highly controllable manner. Due to the reversibility of the phenomenon, the procedure can be repeated for several times. The optomechanical actuation is accurately controlled in a step-by-step manner, by proper manipulation of the number and the intensity of the incident laser pulses. Fluorescence emission measurements of the photochromic molecules in polymers matrices are also presented, to clarify the chemical pathways, which are connected with the optomechanical steps.

1. INTRODUCTION

Recently, there is a rapid development of micro-electro mechanical systems (MEMS) for nanometer scale manipulation, which are build by integration of several components, as cantilevers, micro-actuators, tips and probes, with wiring and external electronics [1]. The manipulation of these components is performed so far by the conversion of electrical energy to mechanical energy. As the dimensions of the MEMS decrease, the control of each individual component independently becomes difficult. An alternative may be their optical manipulation. Lasers seem to be the necessary tools for the optical manipulation of such microsystems since they offer the advantage of the highly controlled and non-contact operation. Our investigation involves fully optically-driven novel sustrates that can be used in the MEMS technology. Herein, we present cantilever-actuators, made of polymers doped with photochromic molecules. They undergo reversible mechanical changes (bending) induced exclusively by their irradiation with laser pulses of selected wavelengths.

We have already demonstrated in previous works that the structural transformations of the photochromic dopants upon irradiation with appropriate laser light induces stresses to their host polymers, which are converted into dimensional changes of the polymeric matrix [2,3]. The photochromic dopant used belongs to the category of spiropyrans, and more specifically it is the indolinospiropyran: 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro [2H-1-benzopyran-2,2'-

---

Corresponding author: A. Athanassiou, e-mail: nassia@iesl.forth.gr
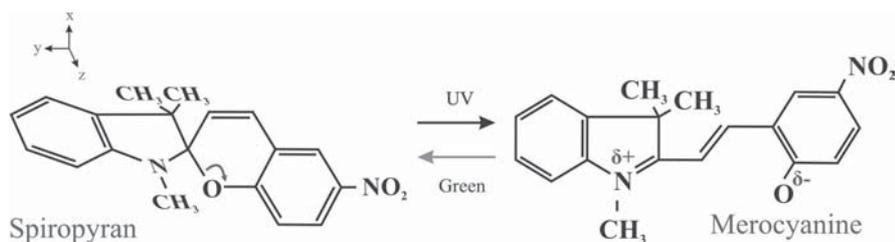
Fig. 1. Reversible transformation between the isomeric forms of the indolinospiropyran dopant induced by appropriate light irradiation.

(2H)-indole] or 6-NO$_2$ BIPS. It is transparent in the visible range of the electromagnetic spectrum, and absorbs in the ultraviolet (UV). By irradiation with UV light it is converted to its isomeric form, merocyanine, through the photochemical cleavage of the C-O bond in the spiropyran ring, as shown in Fig. 1. The merocyanine form exhibits a new absorption band in the visible range of the spectrum. This isomerisation process is reversible. Thus, upon irradiation with light within its visible absorption band the coloured merocyanine form is converted back to the spiro-form [4-6].

The photo-driven cantilevers presented herein are optically thick, freestanding polymer films doped with 5% by wt of the above mentioned spiropyran molecules. The films are mounted onto a stable support, and it is demonstrated that they undergo reversible changes of their dimensions, upon irradiation with laser pulses of 308 nm and 532 nm respectively, following the structural transformations of the incorporated molecules, shown in Fig. 1. The dimensional changes of the polymeric cantilevers are translated into bending. This bending is detected by monitoring the light of a He-Ne laser deflected by the free edge of the cantilevers. The reproducibility of the effect is also investigated by monitoring the reversible movement of the cantilevers for several cycles of UV-green irradiation. Fluorescence emission measurements of polymer films doped with the same dopant concentration as in the case of the cantilever experiments are also presented herein. The fluorescence recording is performed using a 'weak' laser beam to probe the photoproducts previously created by irradiation with UV and subsequently visible light. These experiments elucidate the pathways of the transformations of the photochromic dopants during the photoinduced cycles. A correlation of these results with the reversible

photoinduced movement of the cantilevers is attempted in order to explain the mechanisms, which are responsible for the mechanical effects upon different laser irradiation conditions.

2. EXPERIMENTAL SECTION

2.1. Preparation of the samples

For the preparation of the films used as cantilevers, solutions of the polymer polyethylmethacrylate-co-methylacrylate (PEMMA) (Aldrich) and 5.0% by wt of the photochromic molecule 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro [2H-1-benzopyran-2,2'-(2H)-indole] (6-NO$_2$-BIPS) (Aldrich) are prepared in toluene. A certain volume of this solution is cast on a glass substrate and is allowed to dry in the dark under ambient conditions for ten days to ensure complete removal of toluene. After drying, the sample is immersed into water, which causes the film to be detached from the substrate and float on the water surface. The freestanding film is then left to dry for few hours. The film thickness is in the range of 80 to 200 μm (at least ten times greater than the optical penetration depth of the UV light into the films). For the construction of the cantilever, the film is precisely cut and then fixed onto a stable support, leaving an area of 2.0×3.0 mm^2 of it to stand freely and operate as cantilever. For the preparation of the films for the fluorescence experiments the same solutions as in the case of the cantilevers preparation are used. Only this time the volume of the solution that is cast on the substrate is reduced to ensure optically thin samples (5-8 μm as measured with a profilemeter). Furthermore, quartz substrates are used and the photochromic-polymer films are not detached from them. The solvent-drying procedure remains the same.

2.2. Experimental procedure

For the generation of dimensional changes to the samples two different lasers are used. The first, a XeCl laser operating at 308 nm, $\tau_{pulse} \approx 30$ ns (Lambda Physik, EMG 201 MSC) is used for the spiro-to-merocyanine transformations. The second, an Nd:YAG laser operating at its second harmonic, $\lambda = 532$ nm, $\tau_{pulse} \approx 5$ ns (B. M. Industries, Serie 5000), is absorbed by the formed merocyanine isomers and results eventually into the return of the sample to its initial condition. The film is left to relax for few seconds after the termination of UV irradiation, just before the initiation of green irradiation. The laser beams are focused weakly onto the front surface of the film, so that the entire surface area of the film is homogeneously irradiated (spot area: 2.0×3.0 mm^2). The incident laser radiation is absorbed within the upper layers of the film (≤ 10 μm), while the rest of the film remains unaffected. The dimensions of the laser-affected layers change due to the structural transformations of the photochromic molecules incorporated in these polymer layers. The remaining unaffected layers are dragged by the transformed ones, causing an overall bending of the film. The bending of these photodriven cantilevers is detected by monitoring the light of a cw He-Ne laser, which is deflected by the backside of the photochromic-polymer cantilever. The spot diameter of the He-Ne laser beam on the film is 0.5 mm, and it is incident on the sample towards its freestanding edge at an incidence angle ~ 10-20° to the normal to the surface. A video camera is used for monitoring the movement of the deflected beam on a graduated surface, simultaneously with the laser light irradiation. The graduated surface is placed opposite to the cantilever and few tens of centimetres away.

In the fluorescence experiments, the lasers used to induce the transformations between the different photochromic isomers are a nanosecond XeCl excimer laser operating at 308 nm, $\tau_{pulse} \approx 30$ ns (Lambda Physik, LPX 300) and a dye laser operating at 540 nm, $\tau_{pulse} \approx 30$ ns (Lambda Physik, LPD 3000). The UV laser beam is weakly focused almost perpendicularly onto the sample in a spot of 1.2 mm diameter, using a quartz spherical lens ($f = +500$ mm). The green laser beam is also weakly focused onto exactly the same area where the UV beam is focused, almost perpendicularly to the sample. Irradiation of the samples is performed in ambient atmosphere. In many cases the several experimental cycles are performed on the same spot of the samples to check the reproducibility of the results. In all cases, photoproduct fluorescence is induced by excitation with 308 nm laser pulses of very low fluence ($F_{LASER} \leq 4$ mJ cm^{-2}) to ensure that photoproduct formation by this beam is negligible, and that the recorded fluorescence is derive exclusively from photoproducts formed by the previous 'high fluence' pulses. The weak beam irradiates the sample few seconds after the end of the laser pulse, which induces the photochemical transformations, to ensure that all possible metastable isomers have turned into the final more stable isomers. The alignment of the beams makes sure that the probing/excitation is performed exactly on the affected area. The emission spectrum induced by the probe beam is recorded on an optical multichannel analyser. The description of the fluorescence recording system is described in details elsewhere [7].

3. RESULTS AND DISCUSSION

3.1. Light-induced actuation of photochromic-polymeric cantilevers

The reversible movement of the prepared photochromic-polymeric cantilevers is activated by their irradiation with UV laser pulses followed by green laser pulses. Upon a UV-green irradiation cycle the dimensions of the polymer matrix change in a reverse manner, within the depth that the laser light is absorbed. These changes are translated into a reversible bending of the cantilever, as described in the methodology section. The irradiation cycle terminates when the mechanical actuation of the cantilever stops, after its recovery to the initial position or close to it. The reproducibility of the mechanical cycles of the samples is examined by repeating several irradiation cycles on each one. The movement of a cw He-Ne laser beam deflected by the freestanding edge of the backside of the cantilevers demonstrates the fully optical and reversible dimensional changes of these substrates. Fig. 2 demonstrates the displacement steps of the He-Ne beam deflected from a cantilever made of 5.0% by wt 6-NO$_2$-BIPS in PEMMA vs. the number of laser pulses. For the irradiation were used 10 UV pulses (308 nm) of ~35 mJ cm^{-2}, followed by 200 green pulses (532 nm) of ~75 mJ cm^{-2}. Further irradiation with more than 200 green pulses does not induce any additional changes to the dimensions of the sample. The fluences used are very well below the corresponding ablation thresholds. The repetition rate of the laser pulses is 2 Hz for the excimer laser and 10 Hz for the Nd:YAG laser. The thickness of the cantilever is 80 μm. The optical penetration depth,
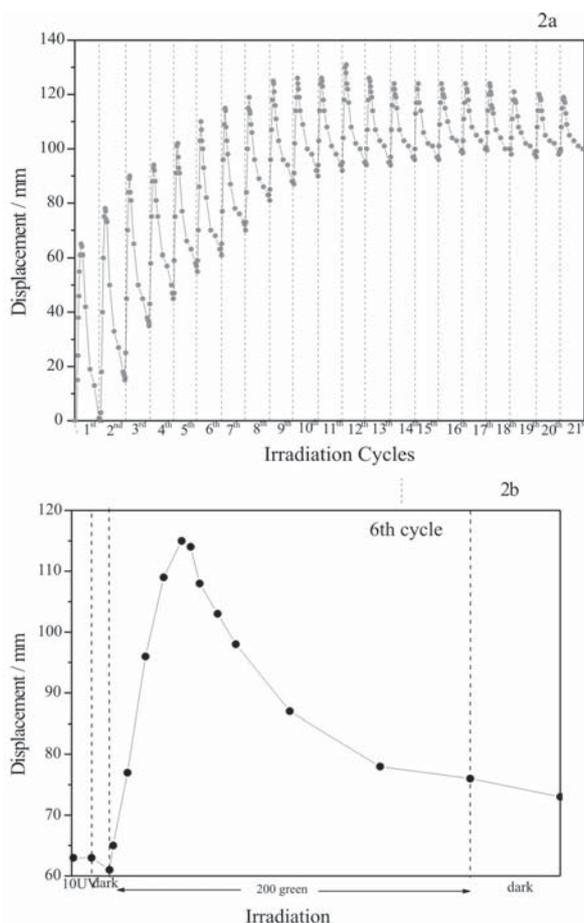
Fig. 2. (a) Successive displacement cycles of a He-Ne beam deflected from the freestanding edge of a photochromic-polymeric cantilever, following the irradiation of the cantilever with successive UV (308 nm) and green (532 nm) laser pulses; (b) Sixth displacement cycle in detail.

of the 308 nm pulses into the PEMMA films doped with 5.0% by wt 6-NO_2-BIPS, is close to 10 μm, as calculated after absorption spectra measurements. Thus, only a layer of $\leq$ 10 μm of the film is significantly affected by the laser light irradiation, and changes its dimensions due to the photochromic transformations. This layer drags the remaining unaffected layer of ~ 70 μm, resulting into the bending of the film. The direction of the deflection of the He-Ne beam, shown in Fig. 2 indicates that the laser affected layer of the samples *contracts*.

In detail, Fig. 2a shows twenty-one repetitions of the optomechanical cycle of the same cantilever, and its reversible optically induced mechanical actuation is nicely demonstrated. At the end of each cycle the sample relaxes either before its initial position, or as it reaches it. As the irradiation cycles are repeated the cantilever shows a mechanical fa-

tigue demonstrated in Fig. 2a by the reduction of the maximum displacement of the deflected beam, and by the fact that it does not return every time at its starting position. After 9-10 irradiation cycles the amplitude of the displacement seems to reach a plateau. Therefore, at this point the mechanical effect becomes fully reversible. The maximum length reduction is obtained at the first optomechanical cycle and it is calculated that it corresponds to about 0.14 % relative contraction of the polymer matrix. When the amplitude of the mechanical cycles is stabilised, the relative contraction of the polymer is decreased to 0.05 %.

As shown in Fig. 2b, the bending of the polymeric cantilever occurs almost exclusively upon irradiation with green laser pulses. The preceding ten UV laser pulses induce only an insignificant bending to the cantilever, and thus, the deflected beam remains almost still. However, when the samples are irradiated exclusively with green pulses, without any previous UV irradiation, no movement occurs. This observation indicates that the initial UV laser pulses induce the transformation of the spiropyran molecules to some merocyanine stereoisomers (colouration process). This transformation process is essential for any following mechanical alterations of the sample (upon green light absorption), but itself does not contribute significantly to the length alterations, and thus to the bending of the cantilever. The observed contraction of the samples upon visible light irradiation can be ascribed to the interconversion of the different merocyanine molecules upon light absorption. Indeed, as mentioned by Görner, in principle, eight merocyanine stereoisomers, with respect to the three partial double bonds, exist (the *cis* isomers: TCT, TCC, CCT, CCC, and the *trans* isomers: TTT, TTC, CTC, CTT) [7]. It is reported many times in the literature that the photoprocesses of the related merocyanines involve several stereoisomers, which convert to the most stable form(s) [7-9]. The stable form(s) depends each time on the host medium. In the present experiment, the energy of 2.3 eV given to the merocyanine isomers by irradiation at 532 nm is enough to exceed the activation barrier height for their conversion back to the spiropyran form, but also to convert them to the other merocyanine stereoisomer(s) [9]. It can therefore be concluded that the mainly responsible procedure for the contraction of the cantilevers is the absorption of visible light from the merocyanine isomers, previously formed upon UV irradiation, which leads either to their subsequent conversion to other merocyanine isomers, or to their interactions.
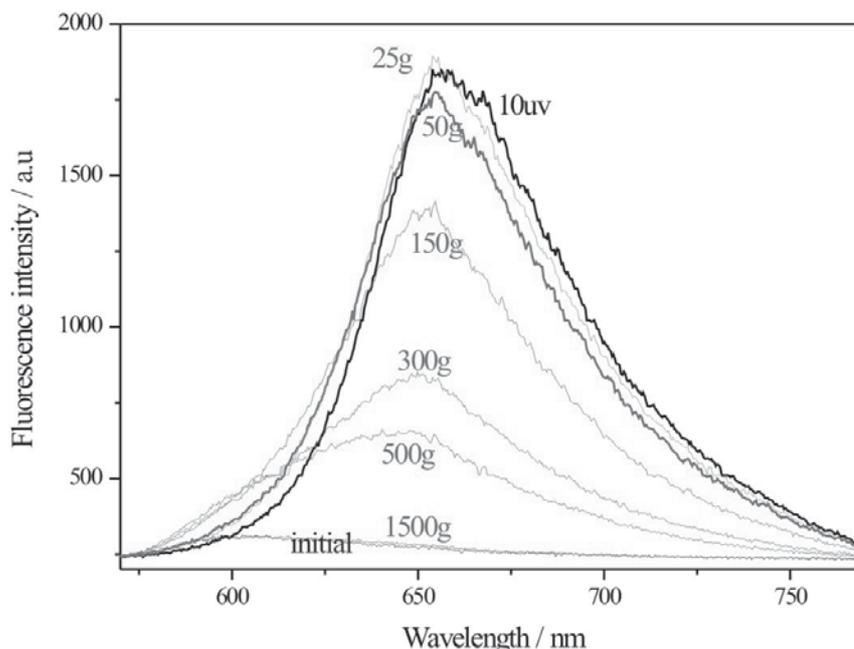
Fig. 3. Fluorescence spectra from 5.0% by wt 6-NO$_2$-BIPS in PEMMA films after irradiation with subsequent UV (308 nm) and green (540 nm) laser pulses.

The experiment presented in Fig. 2 was repeated using this time at each irradiation cycle 10 initial UV pulses of higher fluence (75 mJ cm^{-2}). In this case it was found that bending was induced to the cantilevers already upon UV irradiation. Therefore, UV pulses of 'high' fluences induce an initial contraction to the irradiated samples. The contraction of the samples upon UV laser light irradiation, when higher UV fluences are used, can be ascribed to the absorption band that the merocyanine isomers exhibit in the UV region [2, 10]. Therefore, in this case the UV photons are not only responsible for the initial colouration process of the spiropyran molecules, but also for the following interconversion between the merocyanine molecules.

In Fig. 2 it can be observed also that the cantilever starts returning towards its initial position in each cycle after its irradiation with a certain number of green laser pulses (50-60). This result can be interpreted following the previous argument that the interconversions/interactions of the merocyanines are responsible for the contraction of the samples, assuming that in the first 50-60 green pulses these procedures are dominant. Further irradiation with green laser pulses leads towards the structural restoration of the host matrix, possibly due to the conversion of the merocyanine isomers back to the initial spiropyran form. Smets *et al.* [11] were the first to report the importance of the interconversion of

the merocyanine forms, in the photomechanical effects of polymer films cross-linked with spirobenzopyran compounds. In their experiment, the samples were irradiated with UV lamps for few minutes, followed by irradiation with visible lamps for few more minutes, and then the recovery of the samples was followed in the dark. The contraction of the samples upon UV irradiation was weak, whereas on further irradiation with visible light a sharp increase of contraction was observed. Visible light, which causes the main mechanical transformation, is responsible for the photochemical interconversion of the different merocyanine molecules. This behavior of the samples is identical with the one that we observed using UV laser pulses of low fluence. In another work by Pieroni *et al.* [12] is supported that the driving forces for the photoinduced conformational changes to the host matrix are not simply the interconversions between the merocyanines, but the interactions between them. They mention that when the merocyanine units form dimeric species the structure of the host matrix is strongly affected. To this end, spectroscopic measurements are in progress to investigate the mechanisms behind the mechanical changes of the host matrices. The first fluorescence emission results are presented here in the next section.

3.2. Fluorescence emission from photochromic-polymer samples

To elucidate the pathways of the transformations of the photochromic dopants during the photoinduced mechanical cycles, fluorescence emission experiments are performed. Fig. 3 shows the fluorescence emission of the merocyanine isomers, formed during one irradiation cycle of a film 5.0% by wt 6-NO_2-BIPS in PEMMA. The sample is irradiated with 10 UV pulses (308 nm) of ~35 mJ cm^{-2}, followed by green pulses (540 nm) of ~75 mJ cm^{-2}. The repetition rates of the excimer and the dye lasers are 2 Hz and 10 Hz respectively. The thickness of the film is 7.0 μm and is optically thin. Therefore, the values of fluorescence intensity can be considered to be exactly proportional to the merocyanine isomers formed in the sample, without the need for "inner-filter" effect corrections (self-absorption).

Initially, the sample does not fluoresce, since the incorporated in the polymer matrix molecules are the non-fluorescing spiropyrans [7]. The UV laser pulses are responsible for the initial photochemical cleavage of the C-O bond in the spiropyran ring and for the conversion of the doped-molecules to different merocyanine isomers. The formed isomers after irradiation with 10 UV pulses show a characteristic fluorescence spectrum, which is demonstrated in Fig. 3. The green laser pulses, which follow the UV pulses, are responsible for the conversion of the already formed merocyanine molecules, to other merocyanine stereoisomers, with different structures, and thus, different fluorescence spectra. This conversion is demonstrated in Fig. 3 as the fluorescence spectra change, and their maxima move towards smaller wavelengths upon irradiation with the first green laser pulses (see 25 green pulses in Fig. 3). After additional irradiation of the sample with >50 green laser pulses the fluorescence spectra not only move even further towards smaller wavelengths, but also they exhibit decreased fluorescence intensity. This decrease is indicative of the return of the open form merocyanine molecules to the closed form, non-fluorescing, spiropyran molecules. It can be seen that after 1500 green pulses the fluorescence spectrum has recovered completely to the initial shape, and therefore it can be concluded that all the molecules, incorporated in the polymer, are converted back to the spiropyran form.

As mentioned in the methodology section, the "weak" beam that probes the fluorescence emission irradiates the sample few seconds after the end of the laser pulse, which induces the photochemical transformations. This ensures that all the photochemical procedures in the samples are completed, and thus, the molecules that fluoresce are the finally formed stable merocyanine isomers. Work is in progress with time-resolved fluorescence measurements, to monitor the short-lived merocyanine isomers formed into the laser pulses or in short time periods after them. We expect these experiments to elucidate the pathways of the stereoisomeric transformations into the polymer, and clarify further the role of these transformations and of the interaction between the isomers, to the optomechanical cycles of the photochromic polymers.

Comparing the beam deflection results with the fluorescence emission ones, one may expect the curved cantilevers to be restored after 1500 green pulses, since in the case of the fluorescence emission, the spectrum emitted from the sample after irradiation with this number of green pulses is identical with the initial one. However, it was demonstrated in Fig. 2 that after about 200 green laser pulses the cantilever beams relax close to their starting position. It is therefore obvious that the mechanical effect stops before the complete return of the incorporated photochromic molecules to the spiropyran form. Moreover, the fluorescence intensity maximum reaches a "plateau" between 10 UV and the first few green laser pulses (approximately 50). Despite the plateau of the fluorescence intensity, the spectra change and their "maxima" move towards smaller wavelengths, indicating isomeric transformations upon green light absorption. After approximately 50 green pulses the intensity of the fluorescence starts decreasing, and the spectra move even further, towards the initial one. This decrease of the fluorescence intensity can be very well related to the recovery of the cantilevers after irradiation with 50-60 green laser pulses, confirming the assumption that the mechanical restoration of the polymer is due to the back conversion of the merocyanines to spiropyran.

4. CONCLUSIONS

We present fully optically driven cantilevers made of polymers doped with spiropyran photochromic molecules. Upon appropriate laser light irradiation the cantilevers undergo reversible dimensional changes translated into reversible bending. The colourless incorporated spiropyran molecules upon UV light irradiation are converted into their merocyanine isomers. The merocyanine molecules have an additional absorption band in the visible region. Thus, upon irradiation with visible light they are converted to other merocyanine stereoisomers,

and eventually back to the spiropyran form. This phototransformations of the photochromic molecules seem to induce 'stresses' to their host polymer matrices which are translated into reversible dimensional changes. We demonstrated herein that upon irradiation with UV laser pulses (308 nm) followed by green laser pulses (532 nm), the polymeric cantilevers can be optically actuated reversibly and for several repetitions. The actuation, and in particular the contraction, of the polymeric cantilevers, with the laser fluences used in the presented experiments, occurs almost exclusively upon irradiation with green laser pulses. This observation leads to the conclusion that the transformation of the spiropyran molecules to merocyanine stereoisomers (colouration process) does not contribute significantly to the length alterations. The initial 50-60 green laser pulses are responsible for the length contraction of the samples, whereas subsequent irradiation with green pulses leads towards the recovery of the samples.

Using fluorescence emission measurements from the same photochromic-polymer system we clarify further the pathways of the transformations of the photochromic dopants upon laser light irradiation. Irradiation of the samples with UV laser pulses clearly converts the spiropyran molecules to their merocyanine isomers, since the first are non-fluorescing molecules and the second give a characteristic spectrum. The following green laser pulses interconvert the already existing merocyanine molecules to others, since different fluorescence spectra towards smaller wavelengths are recorded. After additional irradiation of the sample with >50 green laser pulses the fluorescence spectra move even further towards smaller wavelengths and their intensity starts decreasing. This decrease is indicative of the return of the open form merocyanine molecules to the closed form, non-fluorescing, spiropyran molecules. Correlating the fluorescence emission measurements with the dimensional changes of the samples, we conclude that the interconversions of the open merocyanine isomers may play a role in the volume changes of the host matrix. Further fluorescence experiments are in progress to monitor the short-lived merocyanine isomers and their aggregated formed due to their interactions. These experiments are expected to clarify

further the mechanism behind the mechanical effect. Finally, the recovery of the cantilevers can be related to the decrease of the fluorescence intensity, which is due to the return of the open merocyanine forms to the closed spiropyrans.

ACKNOWLEDGEMENTS

REFERENCES

1. N. C. MacDonald, In: *Nanotechnology,* ed. by G.L. Timp (Springer-Verlag, AIP Press, New York, 1999).
2. A. Athanassiou, K. Lakiotaki, V. Tornari, S. Georgiou and C. Fotakis // *Appl. Phys. A* **76** (2003) 97.
3. A. Athanassiou, K. Lakiotaki, M. Kalyva, S. Georgiou and C. Fotakis // *Laser Physics* **13** (2003) 664.
4. M. Levitus, M. Talhavini, R. M. Negri, T. D. Z. Atvars and P. F. Aramendia // *J. Phys. Chem. B* **101** (1977) 680.
5. A. K. Chibisov and H. Görner // *J. Photochem. Photobiol. A* **105** (1997) 261.
6. E. A. Gonzalez-De Los Santos, M. J. Lozano-Gonzalez and A. F. Johnson // *J. Appl. Polym. Sci.* **71** (1999) 259.
7. A. Athanassiou, E. Andreou, D. Fragouli, D. Anglos, S. Georgiou and C. Fotakis // *J. Photochem. Photob. A* **145** (2001) 229.
8. H. Görner // *Chem. Phys.* **222** (1997) 315.
9. Y. Abe, R. Nakao, T. Horii, S. Okada and M. Irie // *J. Photochem. Photobiol. A* **95** (1996) 209.
10. J. Hobley, V. Malatesta, R. Millini, L. Montanari and W. O'Neil Parker // *Phys. Chem. Chem. Phys.* **1** (1999) 3259.
11. A. Tork, F. Boudreault, M. Roberge, A. M. Ritcey, R. A. Lessard and T.V. Galstian // *Appl. Optics* **40** (2001) 1180.
12. G. Smets, J. Braeken and M. Irie // *Pure Appl. Chem.* **50** (1978) 845.
13. O. Pieroni, A. Fissi, N. Angelini and F. Lenci // *Acc. Chem. Res.* **34**, 9-17, 2001.