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► **To cite this version:**

Régis Barille, Peyman Tajalli, Stanislaw Kucharski, Ewelina Ortyl, Jean-Michel Nunzi. Photoinduced deformation of azopolymer nanometric spheres. *Applied Physics Letters*, 2010, 96 (16), pp.163104. 10.1063/1.3409123 . hal-01389328

**HAL Id: hal-01389328**

**<https://hal.science/hal-01389328>**

Submitted on 8 Oct 2021

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## Photoinduced deformation of azopolymer nanometric spheres

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(Received 10 February 2010; accepted 3 April 2010; published online 20 April 2010)

Nanometric spheres of an azopolymer are obtained by micellization from a solution. We observe photoinduced deformation of the individual nanospheres under white light illumination. The diameter expands up to 35% parallel to the substrate surface. The magnitude of the force that is necessary to produce the same effect is estimated. © 2010 American Institute of Physics.

[doi:10.1063/1.3409123]

Azobenzene chromophore containing materials are studied since a long time<sup>1,2</sup> and currently continue to capture researcher's attention.<sup>3</sup> Substantial changes in material properties during light irradiation were investigated. The potential of these materials as active components for a variety of applications from holography to nonlinear optics was studied. The mechanism involved in these photoinduced changes involves the photochemical excitation of the azobenzene group that undergoes a trans to cis isomery and then relaxes back to the trans state with some energy dissipation. By repetition of trans-cis-trans isomerization cycles, a substantial portion of the initially homogeneous distribution of azobenzene groups escapes from its initial position. A large scale mass transport phenomenon occurs and results in surface relief gratings as well as various materials' modifications.

In usual experiments, an azopolymer film is illuminated by an interference pattern, inducing a directed mass migration effect, resulting in a surface pattern consisting in micrometer deep stripes that are stable over long time periods. It was shown more recently that a self-organized structuration effect could be achieved using a single laser beam with controlled polarization.<sup>4</sup> The phenomenon was also observed by using near-field optical techniques in which surfaces could be patterned with a resolution much smaller than the optical wavelength.<sup>5</sup> Further studies demonstrated that the use of an incoherent light source was also efficient in printing a well organized pattern at the surface of an azopolymer thin film.<sup>6</sup> Li *et al.*<sup>7</sup> have decreased the size of the surface exposed to light by using colloidal spheres of azopolymer. Light irradiation could deform the azopolymer colloidal nanospheres. In view of the above previous results we used incoherent white light to induce the azo molecules' motion and to distort nanometer polymer spheres.

Nanospheres are fabricated from a highly photoactive azobenzene derivative containing heterocyclic sulfonamide moieties: 3-[[4-[(E)-(4-[(2,6-dimethylpyrimidin-4-yl) amino] sulfonyl]phenyl) diazenyl]phenyl]-(methyl)amino]propyl 2-methylacrylate. Characteristics of the polymer (inset in Fig. 2) are  $M_n=10750$  Da,  $M_w=15800$  Da, glass transition temperature  $T_g=344.1$  K,  $\lambda_{\max}$

$=448$  nm, absorbance ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )  $\log_{10}(\epsilon)=4.38$ .<sup>8</sup> The azopolymer was dissolved at 50 mg/ml in tetrahydrofuran (THF). The nanospheres were prepared following the method used for aggregate formation from polystyrene-poly(acrylic acid) block copolymers micelles.<sup>9</sup> Deionized water was added dropwise into the THF solution. When micellization occurs, the nanospheres are dropped on a glass substrate. Density of the nanospheres on the surface is about  $9 \mu\text{m}^{-2}$ . Figure 1 presents a scanning electron microscope (SEM) image of the nanospheres dispersed on the surface of a microscope glass slide. We can estimate their external diameter by statistical analysis of the image (Fig. 2): it is  $84 \pm 10$  nm.

We configured an atomic force microscope (AFM) with an inverted microscope in order to illuminate and probe the nanospheres. A single bulb incandescent lamp with broad continuous spectrum is used to shine the nanospheres. Its light is totally incoherent and its polarization random. The lamp spectrum overlaps the blue absorption band of the azopolymer with peak at 438 nm. Lamp power is set to 2.2 mW at the sample location. A microscope objective with magnification  $\times 40$  (0.6 numerical aperture) focuses the light beam on the sample surface. We calculate a full-width at half-maximum spot size  $\Delta x_{\text{FWHM}}=0.42 \mu\text{m}$ . The sample surface is scanned at the beam spot location with the AFM in the noncontact mode every 5 min. During AFM scan, white light is blocked to avoid multiple reflections from the scanning head.

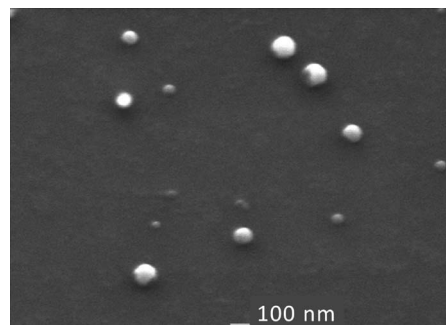


FIG. 1. SEM image of nanospheres dispersed on a glass substrate.

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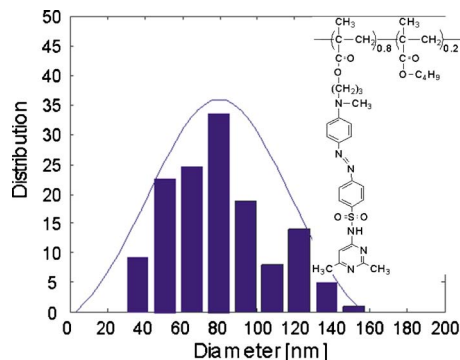


FIG. 2. (Color online) Distribution of nanosphere diameters. Mean nanosphere diameter is  $84 \pm 10$  nm. Inset is the chemical formula of the azobenzene copolymer with 20% butyl-methacrylate monomer ratio.

The white light power was not intense enough onto the sample to melt the nanospheres. Figure 3 shows an AFM image of two nanospheres before and after irradiation of the sample surface with the incoherent white light. Absolute resolution of the image is actually limited by the tip size. After irradiation, the nanosphere width has expanded. Figures 4(a) and 4(b) show a cross section in the horizontal and vertical directions of nanosphere surface profiles before and after irradiation. Spheres expanded almost uniformly in the film plane, with a recorded increase of 20% for the horizontal cross section and 35% for the vertical cross section in the substrate plane (Fig. 4). We attribute the difference to the acentric position of the nanosphere into the beam waist. For exposure times larger than 15 min the morphology of the nanospheres remained stationary. Under the same experimental conditions the results are reproducible from sphere to sphere. We notice also that irradiation pulls the nanospheres upwards. Interestingly, we see the same trend as following the excitation of an azopolymer surface by the evanescent wave from a near-field microscope.<sup>5</sup> The effect is similar also to the irradiation of azopolymer nanotubules.<sup>10</sup>

The uniaxial compression of polymer spheres was studied previously.<sup>11,12</sup> The force  $F$  needed to exert an elastic deformation on an incompressible sphere is derived from Hertz theory which considers the contact deformation of elastic spheres under normal loads in the absence of adhesion and friction. For small deformations, it is as follows:

$$F = \frac{4}{3}GD_0^{0.5}\Delta D^{1.5}, \quad (1)$$

where  $G$  is the elastic modulus,  $\Delta D = D_0 - D$  the deformation,  $D_0$  and  $D$  the initial and final diameters. For poly(methyl-methacrylate) (PMMA),  $G$  is given in the range 1.8–3.1

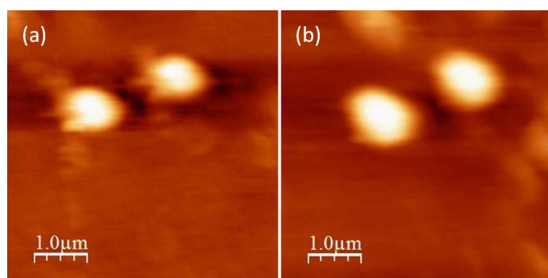


FIG. 3. (Color online) AFM images of nanospheres illuminated by an incoherent white light: (a) before irradiation; (b) after 15 min irradiation under white light.

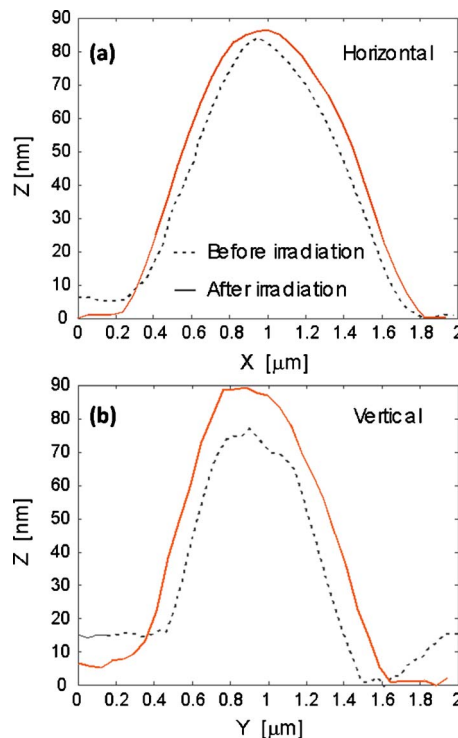


FIG. 4. (Color online) AFM profiles of a nanosphere before and after irradiation with the incoherent white light in the X direction (a) and in the Y direction (b) along the substrate plane.

GPa.<sup>13</sup> Taking the same 1 GPa low bound as Saphiannikova *et al.*,<sup>14</sup> we get the force  $F \approx 1$   $\mu$ N. It is an order of magnitude larger than typical forces needed for the deformation of hollow polyelectrolyte microcapsules using an atomic force microscope,<sup>15</sup> actually the same order as for filled microcapsules, and an order of magnitude lower than the force that was used to indent silicon surfaces.<sup>16</sup> The axial force in the generalized Lorenz–Mie theory (GLMT) is derived within the geometrical optics approximation considering that momentum exchange between the light and the particle exerts an optical force. The axial force in the GLMT is:<sup>17</sup>

$$F_z = \frac{n_m}{c} \frac{2P}{\pi\omega_0^2} C_{pr,z}, \quad (2)$$

where  $C_{pr,z}$  is the cross section for radiation pressure and  $\omega_0$  is the waist radius of the focused beam as defined in Ref. 18. Equation (2) yields an axial radiation pressure force  $F_z \approx 20$  pN, larger than gravity (4.7 pN). Toshchevnikov *et al.*<sup>19</sup> calculated the stress that is exerted on a polymer during surface relief grating formation. It yields a force  $F_z \approx 2$   $\mu$ N onto the nanospheres, rather close to the estimation from Eq. (1).

In conclusion we presented a simple scheme which renders possible the modification of the shape of colloidal particles made out of azopolymers. The photoinduced deformation effect is restricted to a very small surface, which produces a different behavior than in thin films. A white light incoherent beam can be used for mass motion. This light-driven process can be used in photonics and biotechnology applications. The use of polymer nanospheres presents some obvious advantages. For instance, nanospheres permitted to implement a new optical storage principle.<sup>20</sup> Interestingly, it was also shown that as the nanoparticle diameter increases, the interaction area between protein and nanoparticle

increases.<sup>21</sup> Most importantly, whatever the origin of the force that is exerted onto the nanospheres, huge pressure will be transmitted to the interior of the particles or to the surrounding material, a cantilever for instance, opening up the possibility with light to induce and control effectively mechanical motion at the nanoscale.

Research at Queen's University was supported by the Natural Sciences and Engineering Research Council (NSERC RGPIN/327116-2006), the Canada Research Chair program on Chiral Photonics and the Canada Foundation for Innovation (Contract No. 203212).

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