Photocontrollable Deformations of Polymer Particles in Elastic Matrix

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One of the key challenges of material science currently is the design of multifunctional “smart” materials combining features from both molecular and supramolecular levels. Pursuing the strategy of amplification and transduction of light-induced motion of small molecules (photoswitches) across increasing length scales to macroscopic level, a novel polymer composite based on shape-reconfigurable microparticles is designed. The composite represents soft elastic matrix filled with photoactive microparticles of liquid crystal (LC) polymer bearing azobenzene moieties. Illumination of the composite film with polarized light results in a dramatic deformation of the microparticles such that the initially spherical shape becomes elongated along the direction of light polarization. This shape-shifting of particles is fully reversible and can be achieved by annealing or exposure to nonpolarized light. It is shown that photodeformation of particles is accompanied by photo-orientation of LC molecules and both processes can be controlled independently. The practical relevance of such materials is pointed out by the possibility to control optical properties (birefringence and light scattering) and optomechanical feedback yielding a new class of photoactuators. Overall, the developed material containing microscopic polymer photoactuators demonstrates an effective way of transducing molecular operation towards macroscopic functionality and can be particularly useful for optics and soft-robotics.

1. Introduction

Recently, there has been an increasing interest in studying phenomena associated with transformation of light energy into mechanical motion or work, such as photoactuation.[1–5] The fundamental importance of these phenomena occurring under the action of light, such as photofluidization,[6–11] photomobilization,[6,12,13] formation of surface relief gratings,[14–17] and other complex 3D structures[10,18–24] can help to develop photosensitive materials for versatile applications and will also improve and extend our knowledge in soft matter.

The most extensively studied photoactive materials usually contain azobenzene moieties as the light-responsive unit. The properties of azobenzene such as high quantum yield and reversibility of E–Z photoisomerization, high fatigue resistance, and large changes in molecular shape and dipole moment upon isomerization make it uniquely suitable as an active unit. Molecular shape changes of azobenzene can be harnessed on a macroscopic level by the embedding active molecules into hierarchically organized matter[25] and by confinement of the photoactive material in space, such as, spherical colloids which can self-assemble into 2D and 3D structures (photonic crystals). The preparation and study of spherical micrometer-sized particles based on azobenzene polymers have been reported in a number of recent works revealing the importance for various optical microdevices, photonics, microfluidics, etc.[26–38] It has been demonstrated that polarized light irradiation results in elongation of these particles along the light polarization. Despite the interest to the research area, several issues like the mechanism and reversibility of microscopic shape changes are still elusive. Moreover, there are no reports on the influence of liquid crystal (LC) ordering on the shape-shifting and optical properties of the particles, as well as the operation of microparticles has never been exploited to build materials with macroscopic functionalities.

In the current work, we have developed a novel elastic composite material containing shape-reconfigurable particles based on liquid crystalline polymer. We have used styrene–ethylene–butylene–styrene triblock copolymer (SEBS, Figure 1a) as the elastic matrix which provides large deformation and low mechanical stiffness[39] and does not interfere to the deformation of embedded particles. Another important role of the matrix is its elasticity responsible for the compressive forces experienced by the deformed particles which makes possible the shape to recover. The particles are made of liquid crystal copolymer PAAz0 bearing mesogenic and azobenzene...
photoactive groups (Figure 1a). By combining the photochromism of azobenzene and self-organization of the liquid crystalline phase,[40] we target the enhancement of photo-optical and optomechanical feedbacks of the material. We have fabricated the soft elastic composites contacting active microparticles in two steps, mixing and casting/coating. The composites are easily amenable to mechanical and thermal processing and their properties are dually controllable, by light and by applying mechanical stresses. In our study we focus on the manipulation of the shape of the particles and the internal liquid crystal order using a combination of different external stimuli, such as polarized and nonpolarized light, thermal treatment, and external mechanical forces. We demonstrate that such tunable elastic composites with optically anisotropic particles can be useful for soft robotics such as photoactuators, and for optics and photonics as tunable polarization-sensitive light scattering medium. Furthermore, our work paves the way towards a better understanding of the photofluidization and photodeformation phenomena.

2. Results and Discussion

As the photoactive part of the composite material, we have synthesized copolymer PAAzo which is in a glassy state at room temperature ($T_g \approx 28^\circ C$) and forms nematic phase up to $127^\circ C$. Absorbance spectra of PAAzo is characterized by a peak at 366 nm corresponding to $\pi-\pi^*$ electronic transition of azobenzene and another peak at 450 nm associated with n-$\pi^*$ electronic transition (Figure 1b). It is well-known that the excitation of azobenzene with UV or visible light initiates cycles of $E/Z$ photoisomerization. The structure of the polymer used here is dictated by two important aspects. First, the illumination of such a copolymer with polarized light induces cooperative uniaxial alignment of azobenzene side fragments and non-photochromic mesogenic groups in a direction perpendicular to the polarization plane of the incident light.[40] Second, when the thin polymer film is holographically exposed to visible light its surface becomes periodically corrugated indicating the formation of surface relief grating.[41] The latter confirms feasibility of light-induced mass-transfer or photodeformation processes which is crucial for our material design.

To produce microparticles and to embed them in soft elastic matrix, we use the miscibility of PAAzo with SEBS viscose solutions in toluene. A mixture of these solutions are stirred resulting in the formation of an emulsion stabilized by the dissolved block-copolymer. Evaporation of the solvent yields the soft elastic material filled with a dispersion of individual microparticles with diameter in the range of 1–9 $\mu$m. By the analyzing the optical images we have estimated the size distribution profile of PAAzo particles in composite film (Figure 1c). The mean particles size for the given preparation conditions is of about 2.5 $\mu$m; however, it can be varied depending on the concentrations of the polymers, the stirring speed and time. This easy approach for the fabrication of composite films allows for the straightforward scaling up.

Irradiation of the cast composite film with polarized UV light results in a strong anisotropic deformation of PAAzo particles in the direction of the polarization of the incident light as schematically shown in Figure 2a. Analysis of bright field (BF) optical images before and after exposure (Figure 2b,c) reveals that the mean particles diameter (in the case of elongated particles—the long axis) increases from 2.3 to 3.4 $\mu$m (Figure 2d), which corresponds to $\approx 48%$ of axial strain ($f = (l-d_0)/d_0 \times 100\%$, where $l$ is length of the deformed particle and $d_0$ is diameter of the native spherical particle). Microscopic observation of the deformed particles in polarized light (PL) shows a strong optical anisotropy (birefringence) (inset in Figure 2c), which will be discussed in detail in the following section. It is worth mentioning that similar effect of unidirectional deformation of PAAzo particles has also been observed by using different light excitation wavelengths within the absorbance bands of azobenzene chromophores (Figure 1b), e.g., UV laser light (355 nm) or noncoherent blue light (475 nm) can induce the deformation with comparable rates (Figure S1, Supporting Information).

2.1. The Features of Photoinduced Deformation of Microparticles

In order to get a better insight into the light-induced deformation process of the polymer particles, we have prepared the spin-coated composite layer containing low number of particles. Figure 3a demonstrates how the spherical PAAzo particle deforms gradually into a spheroid or spindle-shaped
particle along the polarization direction of the incident UV light (see also Video S1 in the Supporting Information). After prolonged illumination, at a certain value of axial strain (usually above 100%), the spindle shape of the particle becomes unstable and it collapses into a worm-like shape which is due to a sudden loss of tension in the surrounding matrix normal to the axial deformation (Figure S2, Supporting Information).

Here we should mention that for all further experiments UV exposure has been terminated before the rupture of particles.

The deformation into spindle-like shape has recently been shown for azobenzene-based amorphous polymer.[31] Ichikawa and Nakano[29] observed the transformation of spherical particles of azobenzene-based glasses embedded in agar gel into worm-like or thread-like particles under the light exposure. We

Figure 2. a) Schematic representation of the photodeformation of polymer particles. b,c) Bright field (BF) optical images of the composite before and after irradiation with linearly polarized UV light, respectively. Inset—polarized light (PL) optical image; polarizer and analyzer are indicated by crossed red arrows. d) Distribution of particle diameter before and after exposure. Light intensity ≈1.7 W cm⁻²; exposure time—1 min.

Figure 3. a) BF optical images demonstrating the evolution of particle shape during irradiation with linearly polarized UV light. b) Dynamics of the deformation process for particles of different sizes (intensity: ≈1.7 W cm⁻²). c) The influence of light intensity on particle deformation dynamics (particles size: ≈6.5 µm). Insets—deformation rates versus particle size and intensity of UV light. d) BF optical images of the composite before and after exposure with polarized UV light and following annealing at 60 °C for 5 min which demonstrates reversibility of particle deformation.
have observed a similar behavior when PAAzo particles were dispersed in polyvinylalcohol aqueous solution (see Figure S3 in the Supporting Information). In this case, the light exposure deforms PAAzo bead (d = 3.2 µm) into a polymer thread (l = 32 µm, d = 0.5 µm). The significantly larger axial strain (~900%) can be explained with the fact that the free-floating particles do not experience any mechanical constrains from their surroundings, and the curved thread shape is due to the rotational mobility of the particle interfering with the unidirectional straight deformation.

By studying of the light-induced deformation dynamics for particles of different sizes we have found that the decrease of particle diameter accelerates the deformations (Figure 3b), which is likely due to the compression forces of SEBS opposing the particles deformation. On the other hand the deformation can be significantly speeded up by increasing the intensity of UV light accompanied by the increase of optomechanical stress, as is demonstrated in Figure 3c. The values of deformation rates for both variable parameters are provided in the insets of Figure 3b,c.

It is noteworthy that after the light is switched off, the light-generated shape of the microparticle remains constant over time revealing the shape memory likely due to the glassy state of PAAzo. This behavior is opposite to photoactuation of liquid crystal polymer networks where switching off the light usually results in recovery of the initial shape.[1–5] In the case of developed composites, however, reversibility of shape shifting, which is essential for practical applications, can be achieved either by heating or by illumination with light. As the deformed particle experiences the external compression forces from surrounding SEBS which are highly anisotropic due to the anisotropy of light-induced deformation, it can potentially restore the native (spherical) shape when it is soft enough. Indeed, a simple annealing of the composite film at the temperature (e.g., 60 °C) above the glass transition of PAAzo accompanied with its softening results in deformation of the microparticles back to their initial spherical shape (Figure 3d). The recovery of shape can also be achieved by the irradiation with nonpolarized UV light which also results in isotropic softening of PAAzo (Figure S5a, Supporting Information). Usually shape recovery can be achieved within 1 min of UV exposure with intensity of 2.1 W cm$^{-2}$. However, prolonged nonpolarized UV light irradiation results in isotropic deformation of the particles in the plane of the layer (flattening) due to photo-orientation of chromophores along the light propagation direction[42] and associated compressive stress (Figure S5b, Supporting Information). Recently, Ouhdaira et al. have addressed the reversibility of shape shifting azo-particles by oblique laser exposure with variable polarization and irradiation time.[12] In our case any specific exposure conditions are not needed for particle shape recovery meaning that the actuating particles and elastic surrounding operate synergistically.

Let us consider the impact of large uniaxial deformations of the PAAzo particles on the elastic matrix. Light-induced deformation of azobenzene polymer particles is accompanied with significant deformation of the surface of the composite layer. Figure 4a,b shows BF and atomic force microscopy (AFM) images before and after UV irradiation of the selected spot of composite film with two particles. In the native state one of the particle (A) rises above the surface of film while the other particle (B) is fully embedded within the elastomer film. Upon UV exposure of particle A and B, the ejection of elastomer occurs in the direction of the particle elongation with the formation of “hills” on the polymer surface, whereas the “valleys” are formed in the perpendicular direction. This shape morphing of particles coupled with elastic surrounding is able to perform mechanical work against the elastic forces of the SEBS matrix. The stored elastic force is a key to reversibility of particle deformation as we mentioned above. Therefore the LC polymer particles act as microscopic photoactuators whose operation can be potentially amplified and transduced across increasing length scales providing a versatile tool for state-of-the-art soft-robotics.[43] Being inspired by the fact that particles generate mechanical forces and by previously reported concept of polymer-dispersed liquid crystal elastomers,[44] we have designed polymer actuators controllable by light. The photoactuator is composed from the 50 µm thick film of polydimethylsiloxane (PDMS) coated with the composite layer (~40 µm) containing shape-morphing PAAzo microparticles (Figure 4c, left panel). Placed on a flat surface and irradiated with UV light polarized along the long axis (0.2 W cm$^{-2}$, 30 min), the ribbon bends in the direction of the PDMS layer as it is shown in Figure 4c (right panel). Figure 4d clearly demonstrates that the light-induced bending of photoactuator ribbon (1 mm—width, 8 mm—length) indeed occurs and is associated with unidirectional elongation of the PAAzo microparticles (see BF optical images inserted in Figure 4d). The photodeformed particles create mechanical stress in the composite layer along the axis of the ribbon which in turns makes the ribbon bend. When the ribbon is exposed to nonpolarized light (365 nm, I = 150 mW cm$^{-2}$), the initial flat shape recovers due to recovering spherical shape of PAAzo microparticles (Video S2, Supporting Information).

2.2. Deformation of Microparticles and Molecular Orientation

It is known that exposure of thin films of azobenzene-containing polymers to polarized light results in the orientation of molecules in a direction perpendicular to the polarization plane (Figure S4, Supporting Information).[40,45] By means of optical microscope equipped with reflective objectives and coupled with a UV–vis spectrophotometer we have studied the photo-orientation phenomenon of individual PAAzo particle. Figure 5a demonstrates BF images and polarized absorbance spectra of the particle before and after illumination with linearly polarized light. The noticeable difference in polarized absorbance spectra for orthogonal directions is explained by light-induced orientation of azobenzene groups which is quantitatively characterized by dichroism value of ~0.49 (Equation (1), Experimental Section). As is seen from the polar diagram, the direction of molecular alignment is perpendicular to the long axis of the deformed particle and perpendicular to the polarization plane of incident UV light (Figure 5a).

Thus, photoinduced alignment of side-groups of PAAzo and unidirectional deformation of PAAzo microparticles are orthogonally directed processes which occur on different scales and can be selectively addressed. Indeed, both photo-orientation
and photodeformation processes happen on different time-scales: the photo-orientation is a fast process that takes place within a few seconds, while the microparticles deformation usually develops over several minutes if the same light intensity is used. To prove this we have carried out a qualitative experiment using UV light of different intensities. First, the composite layer was exposed to UV polarized light (1 min, $I \approx 1.7 \text{ W cm}^{-2}$) in order to shape the microparticle (Figure 5b, top and middle panels). It is clearly seen from the behavior of the deformed particle between crossed polarizers that the LC alignment direction is perpendicular to long axis of the particle. Then the deformed particle was illuminated with UV light of considerably lower intensity (1 min, $I \approx 50 \text{ mW cm}^{-2}$) and the polarization plane was rotated by 45° in respect to the particle axis (Figure 5b, bottom panel). As displayed on PL images the second exposure exclusively results in reorientation of liquid crystal molecules inside the particle while its shape is preserved and remains invariable due to low intensity of light and short exposure. The molecular reorientation process inside deformed particle is schematically shown in Figure 5b (on the right side). These findings bring us to important conclusion: the shape of microparticles and molecular alignment inside them can be independently controlled by light which can be useful for optics and photonics. Furthermore it provides additional (optical) functionality to photoactuators based on such composite.

### 2.3. Controllable Deformation of Microparticles by Light and Mechanical Forces

In this section we demonstrate how the shape of microparticles can be controlled and additionally highlight the role of elastic SEBS matrix. As we showed above the elasticity of the SEBS is responsible for reversibility of deformations of the embedded PAAzo particles (Figure 3d). Moreover, the independent control over microparticle shapes and direction of axial deformations can be achieved by UV illumination with spatial resolution. Figure 6a shows PAAzo particles 1, 2, and 3 shaped using UV light polarized at 45°, 90°, and 0° in respect to horizon line, respectively. Such localized exposure allows deforming particles independently. By the repetitive exposure of the sample with UV light polarized at different angles we have managed to redirect the microparticles multiple times and on demand (Figure 6b; Video S3, Supporting Information). Dynamics of this process is presented in Figure S6 in the Supporting Information.
Let us now discuss the alternative way of microparticle shape reconfiguring. Since the composite films are elastic it is easy to manipulate the shape of embedded microparticles by applying mechanical strains. In order to prove this, we have coated a composite layer on top of the PDMS 400 µm thick film as it is difficult to handle free-standing thin films of composite due to their softness. Application of mechanical strains and optical observations has been performed in a home-made setup (Figure S7, Supporting Information). The results of photo- and mechanical tuning of the shape of PAAzo microparticles are summarized in Figure 7. We observed that a polarized UV light illumination of the composite film without external strain leads to the elongation of the particles only up to ≈14% of the axial strain (Figure 7a). The lower axial strain in this case is associated with larger size of particles and lower UV light intensity caused by technical constrains (see the Experimental Section). Irradiation of the film subjected to 70% strain with UV light polarized along the stretching direction induces pronounced particles deformation (Figure 7b). On the contrary, we have found that the shape of the particles remain almost unchanged (only minor deformation along the strain direction has been revealed) when the direction of UV light polarization is orthogonal to the stretching direction (Figure 7c). Thus, the polymer photodeformation in this case is nearly suppressed, whereas, according to optical observation in polarized light (PL image in Figure 7c), the photo-orientation still takes place, i.e., particles become strongly birefringent with uniaxial alignment of liquid crystalline fragments.

The irradiation of strained composite films with nonpolarized UV light is found to induce deformation of the particles

Figure 5. a) Polarized absorbance spectra and polar diagram of the uniaxially deformed PAAzo particle (on top). \( A_\parallel \) and \( A_\perp \) correspond to the absorbance spectra of light polarized parallel and perpendicular to the long axis of the deformed particle, respectively. b) BF and PL optical images demonstrating the selective control over the particle shape and alignment of LC molecules inside the particle. Schematic representation of the particle shape and molecular alignment is on the right panel. All LC molecules are indicated with the same color. Polarizer and analyzer are indicated by crossed red arrows.

Figure 6. a) BF optical image illustrating three differently aligned LC particles. b) BF optical images demonstrating the reorientation of LC particles by sequential irradiation steps with altered polarization direction.
along the strain direction without the photo-orientation of mesogenic groups, i.e., the deformed particles are optically isotropic (Figure 7d). The effect can be explained by photo-softening\textsuperscript{[46]} of microparticles expressed isotropically (in all directions) and further molding of the shape by uniaxially stretched elastic surrounding. If the stain is removed right after nonpolarized UV illumination the deformed particle keeps the shape (Figure S8, Supporting Information), which indicates that PAAzo is in the gassy state even when azobenzene moieties are mostly in \( Z \)-form. Similar effect is observed for the recovery of the particle shape upon nonpolarized light irradiation. The annealing of the strained composite film at 60° C without light irradiation causes the deformation along the stretched direction; however, the microparticles are characterized by multidomain, unaligned nematic structure of PAAzo (Figure 7e). Overall, the combination of external mechanical forces and light provides a freedom in controlling the shapes of the microparticles, the degree and direction of photodeformation, and the direction and quality of the alignment of LC molecules.

### 2.4. Discussion on Possible Mechanism of Particles Deformation

Although there are a number of theories describing a limited set of materials and effects such as asymmetric diffusion model\textsuperscript{[47]} or photoinduced molecular diffusion model,\textsuperscript{[48]} the exact origin and mechanism of the photodeformation and photoinduced mass-transport in azobenzene based materials is still unclear. Here, we report valuable observations that can be used to further develop theoretical models that promote the understanding of the above described mechanisms.

Our experimental results undoubtedly show that inside PAAzo particles two simultaneous processes occur. The first process is the photoinduced mass-transport along the polarization direction of the incident light causing the microscopic deformation, whereas the second process is the rotational diffusion of chromophores and mesogens in the orthogonal direction. Evidently, both processes are initiated by cycles of \( E-Z \) isomerization induced by light. Photoisomerization leads to considerable changes of the molecular shape of azobenzene from rod-like \( E \)-isomer to bent-shaped \( Z \)-isomer and back which can induce conformational mobility of polymer chains similar to the one caused by temperature and referred as photofluidization.\textsuperscript{[7,10,19,34]} It is very unlikely that the photofluidization or significant photoinduced softening due to increase of temperature of the polymer material is accounted for the deformation of the particles since we observe the valuable corrugation of elastic matrix which cannot be achieved by fluidized polymer (Figure 4a). This is also confirmed by the insignificant particle elongation under illumination with light having polarization perpendicular to direction of the external strain applied (Figure 7c). We have also excluded the possible influence of...
reduction of scalar order parameter of LC polymers upon UV exposure since similar deformations of microparticles are produced by visible light generating little amount of Z-azobenzenes (Figure S1, Supporting Information). On the contrary, the experimental data agrees with the building up high local mechanical stresses in azo-polymer upon polarized light illumination which was theoretically predicted by Saphannikova and co-workers and experimentally demonstrated by Santer and co-workers. The concept assumes that the (re)orientation of azobenzene fragments perpendicularly to light polarization leads to the reorientation of polymer backbone due to its strong coupling with side-groups which causes the buildup an anisotropic internal stress. As a result the elongation of polymer chains occurs along light polarization and further leads to material deformation. Here we emphasize that the photoalignment of chromophores indeed is the main driving process of photodeformation. However, since photoalignment is the fastest step (see Figure 5b) another criterion should be satisfied for the development of photodeformation of the polymer. Importantly, the azo-material should be exposed to polarized light for long enough in order to sustain photostationary state which allows macromolecules to experience slow translational motion due to enhanced mobility of macromolecular segments. The latter facilitates the building up of internal mechanical stresses which eventually leads to microscopic deformation of the material. The developed type of composite materials is a versatile tool for the study the phenomenon of light-driven deformation; therefore, as the next step of our research we will thoroughly investigate the process by using monodispersed microparticles and monochromatic light as well as LC polymers of different structures.

2.5. Optical Properties of the Composite Films

Since the shape of PAAzo microparticles and LC alignment can be purposefully controlled by light and mechanical forces, such composite films represent a unique and versatile material for optics. For example, relatively thick composite films can act as an effective light-scattering medium with tunable characteristics. Light scattering from the composite originates from the mismatch of the refractive indices of elastic matrix (1.49 as measured using Abbe refractometer) and polymer PAAzo (=1.60"). Since the photo-orientation process is faster than the photodeformation and both can be addressed selectively, there are two ways to control optical properties of light scattering: (i) by controlling the birefringence of the material and (ii) by controlling microparticles shape. Therefore, by irradiating the composite film with low intensity polarized light, the embedded particles become highly birefringent without shape morphing. As a result, the anisotropy of polarized light scattering can be achieved as it is demonstrated in Figure 8a. The anisotropic scattering arises from the large difference between the extraordinary refractive index of the microparticle and refractive index of the elastic matrix (Figure 8a, left panel). The ordinary refractive index of the microparticle is similar to matrix’ index therefore the intensity of light scattering is suppressed (Figure 8a, right panel). The effect of photoinduced molecular alignment inside the microparticles can also be used to inscribe patterns which are visible in polarized light. By short UV exposure through the photomask (amplitude diffraction grating with a period of 90 µm), we have fabricated the pattern with alternating areas where particles have unidirectional molecular alignment.

Figure 8. a) Images of the composite film irradiated with linearly polarized UV light (5 min, I = 50 mW cm⁻²); images were taken in polarized light (polarization direction is indicated by the red arrow). b) PL optical images of the composite film irradiated with polarized UV light (1 s, 1.1 W cm⁻²) through the photomask with a period 90 µm; polarizer and analyzer are indicated by the crossed red arrows. c) BF optical images of the composite film before and after exposure with polarized UV light (axial strain = 40%). Corresponding laser light scattering patterns are presented in the right bottom corners. The probe laser beam is polarized along the LC alignment direction. T₀ and T₉ indicate the transmittance of the probe light polarized parallel and perpendicularly to molecular alignment in microparticles, respectively.
while in the rest of the particles do not possess any specific molecular alignment (Figure 8b).

As mentioned above the shape of the microparticles provides another means to tune light scattering of the composite. Figure 8c shows optical image of the composite film before and after polarized UV exposure and corresponding light scattering patterns (in the corner of each image) of the laser beam ($\lambda = 660$ nm). It is clearly seen that once particles are photodeformed the initially isotropic scattering pattern (angular width is 14.1°) becomes shape-anisotropic, with long axis perpendicular to the axis of photodeformation (angular widths in orthogonal directions are 16.7° and 8.5°). Moreover, due to the photo-orientation of PAAzo the light scattering depends on the direction of probe beam polarization. This anisotropy was estimated by the measuring the probe beam transmission when its polarization is parallel ($T_{\|}$) and perpendicular ($T_{\perp}$) to LC alignment direction within PAAzo microparticles. It has been revealed that the intensity of scattered light is in almost five times higher when polarization of probe beam coincides with LC molecule alignment (see the values depicted in Figure 8c). Thus, light scattering properties of such composites can be tailored in a complex manner by precise control over the shape of the embedded microparticles and LC alignment, which can be useful as fine adjustable flexible media for different optical devices like random lasers, diffusors, etc.

3. Conclusions

A new composite based on elastomer filled with microparticles of liquid crystal copolymer containing azobenzene fragments has been elaborated and studied. We have demonstrated that the irradiation with polarized UV or visible light induces extreme elongation of spherical particles in a direction parallel to the polarization plane. The uniaxial light-induced deformation is accompanied by the alignment of LC molecules in the perpendicular direction and these two processes can be addressed independently due to the difference in timescales at which they occur. The deformation can be reversed by nonpolarized light exposure or annealing at temperature above glass transition of LC copolymer. Shape recovery is possible because of the release of mechanical strains stored in elastic matrix which molds the particle to its initial spherical shape when it is soft enough. Moreover, the microparticles can easily be reconfigured by the changing direction of UV light polarization. We have demonstrated that external mechanical stress applied to the elastic composite is another effective way to manipulate particle shape. Two practically relevant features of such composite materials have been clearly shown: (i) light-induced deformation of microparticles generate mechanical forces which can be further transduced to macroscopic level in order to drive motility relevant for soft robotics; (ii) fine control over birefringence and shape of microparticles can be used to tailor light scattering which allows considering the composite as tunable materials for optics and photonics. Overall, the developed material displays how photoinduced molecular motion of azobenzene switches can be harnessed by means of hierarchical organization and compartmentalization on different levels towards new materials with macroscopic functionalities.

4. Experimental Section

Materials and Composite Preparation: The copolymer PAAzo with a molar ratio of mesogenic and azobenzene side groups of 1:1 was synthesized by free radical polymerization of appropriate monomers which have been obtained according to previously described procedures. The reaction was carried out in anhydrous benzene in a sealed tube under argon atmosphere with the initiator AIBN (2 wt%) for 100 h at 70 °C. The polymerization was carried out to high conversions. The copolymer was purified by prolonged treatment with boiling methanol followed by drying in vacuum at 50 °C overnight. $M_n$ of PAAzo was about 8.6 kDa ($M_n/M_w = 1.6$) which was measured by GPC using a “Knauer” chromatograph (UV detector, column type “LC-100” with a sorbent 1000 Å; solvent THF, 1 mL min$^{-1}$; 25 °C; polystyrene standard).

Phase transition temperatures were detected by polarized optical microscopy (“POLAM-R-112”) equipped with heating stage (“Mettler FP-86”), as well as differential scanning calorimetry (“Mettler TA-4000”, heating rate 10 K min$^{-1}$).

Elastomer, SEBS-mediprene-500120M (HEXPOL TPE AB, Sweden) was employed as the matrix material. Since the elastomer forms a reversible physically cross-linked network, we assume that there are no chemical reactions with the included filler material (PAAzo).

Nematic copolymer PAAzo was dissolved in minimum quantity of toluene and required amount was added to the toluene solution of SEBS (0.75 g mL$^{-1}$). The resulted concentration of PAAzo in respect to SEBS was 1.5 wt%. Because of incompatibility of these polymers two-phase system was formed. The composite solution was stirred at 500 r.p.m. for 30 min followed by film deposition by casting or spin-coating (800 r.p.m., 2 min) onto a glass or PDMS substrate. The obtained films were dried at ambient conditions before tests. The thickness of spin-coated layers was measured by profilometer as 9–11 µm.

Photoactuators were prepared by casting of toluene solution of SEBS and PAAzo on PDMS (Sylgard 184, Dow Corning) layer of 50 µm thickness. Resulted thickness of the composite layer on top of PDMS was about 40 µm (Figure S9, Supporting Information). PDMS layer was prepared in glass cell with 50 µm gap defined by Teflon spacers.

Measurements: The absorption spectra were measured using a TIDAS spectrometer (J&J). The optical and polarized optical microscopic investigations were performed using a microscope AxiosPlan2 (Carl Zeiss). The surface relief topography was studied by atomic force microscopy (SPM Smena, NT-MDT) performed in the tapping mode.

The optical microscope (Olympus BX51) equipped with reflective objectives, Clan-Taylor prism, and combined with spectrometer (Resultec 2200; Xe-lamp as a light source) was used for the measuring of local polarized absorbance spectra of the individual PAAzo particle. The scanning area was 6 x 6 µm.

The dichroism values, $D$, of the polymer films were calculated from the spectra using the following Equation (1)

$$D = \frac{(A_{\|} - A_{\perp})}{(A_{\|} + A_{\perp})}$$  (1)

where $A_{\|}$ and $A_{\perp}$ are the absorbance parallel and perpendicular to the polarization plane of the excitation light, respectively.

The samples were irradiated directly through the microscope objectives with polychromatic UV-light from a high-pressure mercury lamp (HBO lamp, 100 W, “Osram”). A neutral density filters were used to vary light intensity in the range of 0.2–3.9 W cm$^{-2}$ as measured at 365 nm by a power meter PM-100D (Thorlabs) equipped with thermal power sensor.

The experimental setup for the in situ observation of the light-induced particles shape-shifting in an axially prestrained composite is illustrated in Figure S7 in the Supporting Information. The setup is made of two film-holder units and two micromoving platforms to apply a strain. The experiments were carried out using composite films spin-coated (from 0.1 g mL$^{-1}$ toluene solution, 800 r.p.m.) on elastic substrate with the thickness of 400 µm made of conventional PDMS. Due to the technical constrains, relatively large particles (up to 20 µm) and UV light with intensity of about 0.7 W cm$^{-2}$ were used for this set of experiments.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The research was part of the Advanced Research Center for Chemical Building Blocks, ARC CBBC, which is co-founded and co-financed by the Netherlands Organization for Scientific Research (NWO) and the Netherlands Ministry of Economic Affairs. A.B. acknowledges the support by the Russian Science Foundation (19-13-00029; copolymer synthesis) and Russian Foundation for Basic Research (Grants no. 19-03-00337; study of photooptical properties of composites). The authors acknowledge M. Kollosohe (Potsdam University, Germany) for help with image analysis and fruitful discussions.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
azobenzene, liquid crystal polymers, photoactuators, photo-orientation, shape-shifting particles

Received: September 2, 2019
Published online: September 25, 2019

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