Article

Photochemical Mechanism and Photothermal Considerations in the Mechanical Response of Monodomain, Azobenzene-Functionalized Liquid Crystal Polymer Networks

September 2012 · Macromolecules 45(17):7163-7170
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Authors:

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Citations (70) References (39)

Abstract

The potential for wireless transduction of input light energy into mechanical outputs has led to a reinvigorated pursuit of photomechanical effects in polymeric materials and composites. We report here on factors influencing the photochemical mechanism (and thus the mechanical output) in monodomain azobenzene-functionalized liquid crystal polymer networks. Through systematic examination of a representative material with both mechanics and spectroscopic characterization the prevalence of the trans–cis and trans–cis–trans mechanisms is elucidated. Furthermore, the role of light intensity in generating heat (photothermal effects) is also reported.

Citations (70) References (39)

... In addition, azobenzene moieties have considerable photothermal conversion ability. 33, 34 The photothermal responsive-ness can be greatly enhanced when the applied light intensity I is higher than one critical value. 33 In our case, during exposure to high-intensity light, the exposed PDO 3 film and the underlying PDMS substrate are heated by the photothermal effect of PDO 3 , leading to a significantly increased film temperature T h (e.g., ~87°C in the case of 1.8 W cm −2 light irradiation for 10 s (Figure S5)). ...

... 33,34 The photothermal responsive-ness can be greatly enhanced when the applied light intensity I is higher than one critical value. 33 In our case, during exposure to high-intensity light, the exposed PDO 3 film and the underlying PDMS substrate are heated by the photothermal effect of PDO 3 , leading to a significantly increased film temperature T h (e.g., ~87°C in the case of 1.8 W cm −2 light irradiation for 10 s (Figure S5)). Considering the mismatch in the thermal expansion coefficients between the film and the substrate, an equibiaxial compressive stress σ is generated upon air cooling after irradiation. ...

... Furthermore, once surface wrinkling begins, it seems that λ does not change significantly due to a higher energy barrier encountered in the change of wrinkling wavelength as discussed in previous studies. 40 Considering that T h is determined by the photothermal effect, 33, 34 we further investigated the influence of light irradiation parameters on the wrinkle formation (Figure S6 and Table S1). It is seen that surface wrinkling can only be elicited when the light dose (D = I × t w) exceeds a critical value for a given I or exposure time t w (Figure 2d and Table S1). ...

All-Optical Reversible Azo-Based Wrinkling Patterns with High Aspect Ratio and Polarization-Independent Orientation for…

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... This mechanism is generally called "optical effect" [46] and one example is reported in Figure 3d. [47] When irradiated with UV laser light, the uniaxially aligned polymer, prepared by CL1 and D1, bent toward the control beam as a consequence of the local strain generated by the photoisomerization on the illuminated side. Thanks to the Adv. ...

... Adapted with permission. [47] Copyright 2012, American Chemical Society. e) Deformation of splayed LCNs by photothermal effect: graph of the bending angles at different powers during irradiation at 532 nm for different formulations (MMx where x indicates the % of crosslinker) and optical images of deformations for LCN with 30% of crosslinker (MM30); Adapted with permission. ...

... Moreover, a dose-dependent behavior was demonstrated: a laser irradiation power increase enabled to raise the isomerization yield and therefore the polymer deformation. [47] A different type of photoresponsive mechanism is induced by push-pull azobenzenes, as D2 described by Zeng et al. [45] In this case, the dyes work as nanoscale heaters able to dissipate light energy into heat and thus driving a thermal transition. This effect can be obtained not only by azobenzenes but also by inorganic nanoparticles or dyes with various chemical structures, opening to a wide wavelength range to control the material properties. ...

Self-Regulating Capabilities in Photonic Robotics

Article

Dec 2018

Daniele Martella · Sara Nocentini · Camilla Parmeggiani · Diederik Wiersma

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... To induce a noticeable photomechanical response in azo-containing LC networks, not only the effect of LC dilution upon illumination with the UV light but also strong reorientation effects under the linearly polarized visible light have been successfully utilized [23][24] [25] . For example, the direction of photoinduced bending of the polymer network with azobenzene LC moieties can be reversed by switching the polarization of the laser beam in orthogonal directions [23]. ...

... This result justifies the reasonability of using two-component networks with strong LC interactions to create materials which are able to produce light-induced deformations of large magnitudes. Such photodeformable materials based on LC polymer networks are widely reported in the literature [15,16,[23] [24] [25] [57][58][59][60][61][62][63]. ...

... Two effects can be seen from Figure 7. First, a decrease of the rotational diffusion coefficients D T,M due to an increase of the viscosity leads to slowing down of the light-induced reordering and deformation in the region t < 100τ T . This result of theory explains the tendency observed in many experiments: the characteristic time of photo-orientation and photodeformation increases significantly, from several seconds up to minutes and hours, with the decrease of temperature from the viscoelastic state above T g to the glassy state below T g [15,16,[23][24] [25] [57][58][59][60] [61][62][63]. ...

Kinetics of Ordering and Deformation in Photosensitive Azobenzene LC Networks

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... Liquid-crystalline polymers (LCPs) or Polymer liquid-crystals (Barón 2001, Barón and Stepto 2002) constitute an important class of materials. In the last years they regain the scientific interest especially in relation with the synthesis of bio-inspired and smart materials (Liu et al. 2013, Moritsugu et al. 2011, Ahir et al. 2006, Li C et al. 2012 , Lee et al 2012 . For instance, low surface energy LCPs possessing high hydrophobicity and lipophobicity (Martinelli et al. 2010) or hydrophobicity and oleophobicity (Caillier et al. 2008) are synthesized, mimicking the plant leaf and fruit surfaces. ...

... The most commonly used one for the investigation of LCPs is POM (Fang et al. 2013, Petr and Hammond 2011, Okano et al. 2010, Lockwood et al. 2008, Huang and Shi 2012, Hu et al. 2012, Caillier L et al. 2008, Al-Muaikel and Aly 2013, Wei et al. 2014, Wojtczak M et al. 2014 , Lee et al 2012 . Characteristic POM textures, obtained under cross-polarizers and sometimes wave-plates, result from the well-known optical activity of the PLCs, possessing some degree of order (similar to the crystals) and owing to specific singularities in their order (Collier 1992, Gray andWinsor 1974 structures. ...

Structure and Phase Transitions of Polymer Liquid Crystals, Revealed by Means of Differential Scanning Calorimetry, Real-...

Chapter

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... The magnitude of bending angle depends on cantilever dimensions, irradiation conditions, i.e., intensity of the laser beam, kind of light polarization (perpendicular or parallel to the long axis of the cantilever), and properties of the polymer material resulting mainly from the rigidity of the polymer backbone and the content of azochromophore [20]. The photomechanical effect in azomaterials is generally investigated in liquid crystal elastomers (LCE) [21][22] [23][24], liquid crystals gels [25], crosslinked liquid crystal polymers [26,27], liquid crystal polymers [28,29], and liquid crystal polymer networks [30][31] [32] . This kind of material exhibits large and fast movement of the cantilevers and low stability after turning off the excitation light. ...
... Cause of that, the bending angle (defined as the angle between the line passing through the mounting and tip points and vertical direction) strongly depends on sample geometry (width and thickness) [18,35]. Lee and White [32] showed that photothermal effects can also occur in the liquid crystal (LC) cantilevers when the intensity of the excitation beam is above 110 mW/cm 2 . ...

A short review of the photomechanical effect in azo-containing amorphous (glassy) polymers

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... We suggest that this additional contribution is the consequence of effective molecular oscillations of the crosslinked chromophore between the two isomer configurations during illumination. 31, 45 This oscillation can create dynamic free volume by continuous trans-cis and cis-trans excitation, as both illumination wavelengths are absorbed by both isomeric forms. We speculate that a macroscopic manifestation of these molecular oscillations is only observable in combination with a thermal component, as no macroscopic manifestation of this effect is seen when the films are submerged in water. ...

Unravelling the photothermal and photomechanical contributions to actuation of azobenzene-doped liquid crystal…

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... Upon conversion from the trans to cis forms, the change in azobenzene shape tends to disrupt the local ordering of the surrounding nematic network, resulting in a contraction along the director. Importantly, light absorption and repeated photoisomerization also inevitably generate heat (as will be addressed in detail in Section Dyes), and although photomechanical effects in many azobenzene-functionalized LC materials are largely attributed to isomerization, it can often be difficult to fully deconvolute the photochemical and photothermal contributions to the observed photoresponse [14] . ...

Light-Induced Shape Morphing of Thin Films

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Alexa Kuenstler · Ryan C. Hayward

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... Azobenzene liquid crystals carrying a vinyl group are "reactive mesogens" that can be used to prepare polymers and copolymers also showing liquid crystal and photo-responsive properties [7]. Lee and White employed vinyl-functionalized azobenzene mesogens to synthesize liquid crystal networks (LCN), which were evaluated in their photo-mechanical, photochemical and photothermal responses [8] . García-Amoros et al. used vinyl cyano-azobenzene mesogens (5 wt%) to prepare side-chain liquid crystal elastomers for which the photo-actuation and thermal isomerization mechanisms were studied [9]. ...

Synthesis of vinyl-functionalized azobenzene mesogens and study of their liquid-crystalline behavior

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... [40] Most photochemical materials also respond thermally but not vice versa. [41] Pros and Cons Comparison: Optical materials can be typically much softer (elastic modulus on the order of 10 4 -10 9 Pa) and are more similar to biological tissues so that they can be used to mimic the natural environment for cell growth and muscle functionality. [42] Next, it is much easier to make optical materials biocompatible, where they do not typically need any additional micro/nanomaterials embedded inside or coated outside that are not easy to make biocompatible while having high performance actuation. ...

Pros and Cons: Magnetic versus Optical Microrobots

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... This experimental setup (19) involved posts 75 m in height and 25 m in width that were irradiated with nonpolarized light of intensity 3.5 mW/cm 2 . This intensity is sufficiently low that the response is dominated by photochemical effects, as opposed to photothermal (34) , justifying the omission of heat conduction in our model. Figure 1B provides a schematic of the finite element representation of such a post; we vary the incident angle of light about the two axes indicated in the figure. ...

Twist again: Dynamically and reversibly controllable chirality in liquid crystalline elastomer microposts

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... However, photothermal effect was observed when the light intensity was higher than 100 mW/cm 2 . 39 Effect of Molecular Weight on Light Direction. Similarly, the

molecular weight of the LCBCs also played an important role in the light-directed way. ...

Vertical Orientation of Nanocylinders in Liquid-Crystalline Block Copolymers Directed by Light

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Tianjie Wang · Xiao li · Zhijiao Dong · Haifeng Yu

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... Azo dye-doped liquid crystals and related materials are employed for controllable holographic gratings [22] [23][24]. In addition, the photo-induced isomerization of azo dyes [25] and thus the photo-induced reorientations [26], photo thermal effect [27] , or photo-induced isothermal phase transitions [28] in azo dye-doped liquid crystals are widely studied and applied on non-linear optics, photo alignment, and photo actuators [29][30] [31]. In this work, we present a prototype of electrically controllable diffraction gratings based on liquid crystals. ...

Electrically Controlled Diffraction Grating in Azo Dye-Doped Liquid Crystals

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... In the SmA* phase, LCs are not affected by boundary conditions and are self-aligned vertically because of the unique property of the phase. 31, 32 However, planar anchoring can induce random orientation of the LCs by force competition between the SmA layering ,which favors homeotropic orientation, and surface anchoring which imposes homogeneous orientation. 33 Light scattering occurs because of the refractive index mismatch between domains of the randomly aligned LCs (Figure 2c) and, therefore, can be used as the hazyopaque state of an LC smart window. ...

Self-Regulation of Infrared Using a Liquid Crystal Mixture Doped with Push–Pull Azobenzene for Energy-Saving Smart…

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... 1,2 One of the most explored methods to mediate molecular motion is to embed the photo-active units into the ordered hierarchical assemblies of alternating copolymers or liquid crystal networks. [3][4][5][6][7][8][9] Among photoactive molecules, 10 azobenzenes are widely studied because of their well-known reversible photo-isomerization. 11,12 Upon irradiation with linearly polarized light (LPL), azobenzenes align their transition dipole moment perpendicular to the electric vector (E) of the incoming light by continuous trans-cis-trans photo-isomerization. [13] [14][15][16][17] Using this technique, assemblies of alternating copolymers containing azobenzene moieties in the side chains can be linearly aligned when irradiated with LPL, [14][15][16][17][18][19] and the photo-alignment process has been unraveled in time. [20][21][22] Based on the same principle, irradiation with circularly polarized light (CPL) has been

used to imprint chiral organization into supramolecular structures. ...

Photo-controlled alignment and helical organization in main-chain liquid crystalline alternating polymers

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... This photothermal property has reported previously for an azobenzene-functionalized liquid crystal polymer. 38 Hence, when the D1-doped LLC samples are irradiated, the observed phase changes may be at least partially associated with an actual increase in temperature. ...

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