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Azo Compounds

Enhancement of Photogenerated Mechanical Force in Azobenzene-Functionalized Polyimides**

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Transducing an input energy stimulus into output energy capable of powering or accomplishing mechanical work is a topic of considerable and pervasive interest across many scientific disciplines. Over the course of the last century, the predominant energy source fueling modern society is taken from nonrenewable carbon sources—primarily petroleum and coal. It is no surprise then that harnessing natural and renewable energy sources offer environmentally friendly solutions that have spawned an ever-burgeoning pursuit of novel materials and paradigms to transduce these energy inputs primarily into electricity. This work focuses on harnessing light energy and employs photoresponsive macromolecules to directly convert light into mechanical work, reported here as the photodirected bending of a cantilever or photogenerated tensile stress of a constrained system. Prior work demonstrating solar-powered photomechanical effects in azobenzene-based liquid crystalline polymer networks (azo-LCN) confirm the potential of direct conversion of solar energy into mechanical work.[1,2]

Photomechanical effects in macromolecules were first discussed by Lovrien[3] and viably demonstrated by Agolini and Gay.[4] These works laid the groundwork for subsequent efforts, primarily synthetic in nature, pursuing the development of novel photochromic polymeric materials capable of generating large, optically reversible strain. The work of Eisenbach[5] is typical of the strain cycles achievable in conventional amorphous polymeric materials, that is, realizing approximately 0.25% strain cycles in an ethyl acrylate polymer containing an azobenzene-functionalized side chain. In 2001, Finkelmann and co-workers reported[6] on the realization of photogenerated strain of 20%, which was observed upon UV irradiation of liquid crystal elastomers having azobenzene side chains (azo-LCE). The comparatively amplified strain generated in this azo-LCE was chiefly enabled by the association of the UV-directed conformational changes in the azobenzene side chains and the liquid crystalline order, thus resulting in an isothermal, photoinduced order–disorder transition.[7] Ikeda and co-workers expanded on the work of Finkelmann and co-workers by preparing a glassy liquid crystal polymer network composed entirely of two azobenzene-containing mesogenic monomers (azo-LCN).[8] In the initial work, the material was heated above the glass transition temperature (T_g) of the polymer, and the orientation of linearly polarized UV light to the film directed bending along a number of axes. Exposure to longer-wavelength light reversed the bending, thus restoring the film to the initial flat shape. Subsequent works from the groups of Ikeda,[9–14] Broer,[15–18] and ours[2,19–23] have confirmed that large bending is observable in the glassy state in a variety of azo-LCN materials, and is potentially useful in microfluidics,[18] optics,[24] actuation,[11] and shape memory.[25]

The amplification of the photomechanical response in azo-based liquid crystalline systems is dependent on the state of the material system (rubbery azo-LCE or glassy azo-LCN). In rubbery azo-LCE, the given stimulus (heat or light) reduces the order of the material system, potentially resulting in a phase change. The resulting phase change amplifies the response to the actinic stimulus.[26,27] In contrast, the order of glassy azo-LCN systems during irradiation does not significantly change,[17] and the initial mesophase is maintained. Thus, the photomechanical responses observed in glassy azo-LCN should not depend on the system exhibiting liquid crystallinity. This was recently confirmed in a report detailing large bending of cantilevers composed of glassy, crosslinked polyimides functionalized with azobenzene (non-liquid-crystalline).[28] Exposure of these cantilevers to blue-green irradiation ($\lambda = 442$ nm in this case) yielded polarization-directed forward and reverse bending that was nearly identical to that observed in glassy azo-LCN having a polydomain orientation.[19,29]

The photomechanical output of a given material system is a product of thermomechanical and optical properties as well as the sample geometry. Photoinduced bending, twisting, or uniaxial contraction and expansion of azo-LCN and other photoresponsive macromolecular systems are ultimately a manifestation of the interplay of these variables—predictable from an understanding of viscoelasticity, optics/photochemistry, and mechanics. This work primarily focuses on the cantilever geometry. Bending is observable in cantilevers subjected to a strain gradient. In photoresponsive systems with sufficient absorption coefficients (such as the polyimide materials examined here) a strain gradient naturally arises, which mirrors the penetration (absorption) profile of light across the cantilever thickness. The radius of curvature (bending angle) for photoinduced bending of a cantilever is independent of modulus and simply a product of geometry (cantilever thickness, width) and the photogenerated strain.[17]

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Thus, a cantilever geometry allows the thermomechanical properties (such as modulus) to be decoupled from the resulting bending (e.g. photogenerated strain).

We report on the photomechanical response of a series of linear polyimides and co-polyimides that contain main-chain azobenzene units and span from amorphous to semi-crystalline. These materials exhibit a considerable increase in both T_g values and modulus relative to those of the crosslinked, azobenzene-functionalized polyimides (azo-PI) and azo-LCN previously examined. We begin by briefly summarizing the preparation of the materials before moving onto an examination of the photomechanical response of the materials in bending as well as in tension. The relationship of crystallinity and photomechanical response is supported by X-ray diffraction and density experiments. As with previous examinations of azo-LCN[19,29] and azo-PI[28] this work employs blue-green irradiation to allow all-optical control of forward and reverse bending (or contractile and expansive stress) by adjusting the orientation of the linear polarization of the irradiating light. Blue-green irradiation is known to induce *trans–cis–trans* reorientation of azobenzene chromophores. This reorientation phenomena has been documented in a variety of polymeric systems, including some at more than 300 °C below the T_g value,[30] in the generation of volume and surface relief gratings[31,32] in azobenzene polymers. Confirmation of this mechanism in glassy azo-LCN materials has been recently published.[19]

The series of linear polyimides examined here was prepared by polymerizing 4-4′-diaminoazobenzene[33] (DAAB, **1**) with either the structurally rigid pyromellitic dianhydride (PMDA; **2**) or the more flexible dianhydride 1,1,1,3,3,3-hexafluoro-2,2-bis(4-phthalic anhydride) propane (6FDA, **3**) to form statistical copolymers (see Scheme S1 in the Supporting Information). The resulting polyimides are designated as azo-PI-PMDA,[4] azo-PI-6FDA,[34] and azo-coPI-xx where xx corresponds to the percentage of PMDA with respect to 6FDA in the copolymer (Table 1). It was expected and confirmed with wide-angle X-ray diffraction (Table 1, and Figure S1 in in the Supporting Information) that the azo-PI-6FDA material is amorphous whereas the azo-PI-PMDA material is semi-crystalline. The degree of crystallinity (crystallinity index) increases with PMDA concentration in the co-polyimides (azo-coPI-25, azo-coPI-50, and azo-coPI-75; Table 1, and Figure S1). Notably, the T_g value (360 °C to >450 °C) and storage modulus (E′; 3.8–6.2 GPa), both summarized in Table 1, of these materials greatly exceed those of the previously examined glassy azo-LCN[29] or crosslinked, azobenzene-functionalized polyimides.[28] The increase in T_g and modulus values with increasing crystallinity is expected.[35,36]

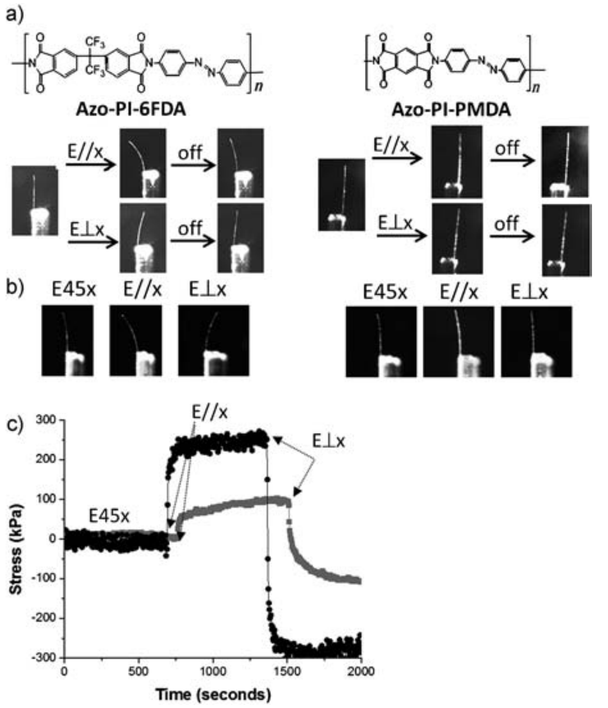

Figure 1. Polarization-dependent photomechanical response of azo-PI-6FDA upon irradiation with 100 mW cm^{-2} of $\lambda = 442$ nm light (a) and azo-PI-PMDA upon irradiation with 100 mW cm^{-2} of $\lambda = 488$ nm (b). The light was polarized parallel to the long axis (E ∥ x) of the 5 mm × 0.5 mm × 0.02 mm cantilever and orthogonal to the long axis of the cantilever (E ⊥ x). c) The tensile stress generated from azo-PI-6FDA (●) and azo-PI-PMDA (■) upon irradiation with 100 mW cm^{-2} of $\lambda = 457$, 488, and 514 nm multiline output from an Argon ion laser is examined during continuous irradiation to linearly polarized light oriented 45°, parallel, and orthogonal to the long axis of the 6 mm × 1 mm × 0.02 mm gauge.

The photomechanical response of the amorphous azo-PI-6FDA and the semi-crystalline azo-PI-PMDA are contrasted in Figure 1. Irradiation of the 5 × 0.5 × 0.02 mm cantilever composed of azo-PI-6FDA (Figure 1 a) with 100 mW cm^{-2} $\lambda = 442$ nm light, which is polarized parallel to the long axis, causes bending to 26° in approximately 60 minutes. Reversing the orientation of the linear polarization of the $\lambda = 442$ nm irradiation reverses the bending direction of the cantilever, thus eventually bending to −15°. Upon removal of the light, the film partially fixes with the cantilever remaining at an angle of 14° and −9° (measured after three days). A cantilever composed of azo-PI-PMDA and subjected to identical exposure conditions (Figure 1 a) does not bend upon irradiation with $\lambda = 442$ nm in either polarization orientation.

Table 1: Summary of composition and nomenclature of azobenzene-functionalized polyimides and co-polyimides examined in this work.

Sample code	**1** [mol %]	**2** [mol %]	**3** [mol %]	ρ [g cm^{-3}]	T_g [°C][a]	E′ [GPa][b]	x [%][c]
Azo-PI-6FDA	50	0	50	1.428	362	3.80	0
Azo-coPI-25	50	12.5	37.5	1.430	373	3.87	2.5
Azo-coPI-50	50	25	25	1.432	379	4.12	2.6
Azo-coPI-75	50	37.5	12.5	1.446	411	4.94	15.3
Azo-PI-PMDA	50	50	0	1.465	>450	6.12	35.5

[a] Determined from the peak value of tan δ curve. [b] Storage modulus obtained from DMA. [c] Crystallinity index obtained from X-ray measurement.

The photomechanical response was also examined in tension by placing the materials (6 × 1 ×

0.02 mm) in a strain-controlled dynamic mechanical analyzer (DMA, TA Instruments RSA III). The films were held with a 4×10^{-5}% strain to pretension the film. The furnace of the DMA was left open to allow irradiation with an Argon-ion laser beam composed of $\lambda = 457$, 488, and 514 nm light. As shown in Figure 1 b, azo-PI-6FDA and azo-PI-PMDA exhibit the same trends in the photoresponse upon illumination with linearly polarized $\lambda = 488$ nm irradiation as $\lambda = 442$ nm irradiation (where E45x indicates polarization aligned 45° to the long axis of the cantilever). In the tensile experiment, the films were initially exposed to the blue-green light polarized 45° to the long axis of the gauge. As evident in Figure 1 b, no bending is observed for either material upon irradiation with this wavelength at this polarization angle. Similarly, both azo-PI-6FDA and azo-PI-PMDA do not generate stress to this exposure condition (Figure 1 b). As with $\lambda = 442$ nm exposure, the cantilevers composed with azo-PI-6FDA bend bidirectionally upon exposure to $\lambda = 488$ nm light while the azo-PI-PMDA material is not responsive. In the tensile experiment, when the polarization is rotated (under continuous irradiation) such that it is parallel to the long axis of the gauge the materials exhibit a contractile stress of 260 kPa (azo-PI-6FDA) and 100 kPa (azo-PI-PMDA). Rotation of the polarization of the irradiating source so that is orthogonal (once again, under continuous irradiation) to the long axis of the gauge, results in expansive stress of 265 kPa and 105 kPa. Importantly, the sign of the stress matches the expected results from the bending reported in Figure 1 a. In contrast to previous examinations of stress in azo-LCN materials when exposed to blue-green[37] irradiation, the stress of approximately 260 kPa is an enhancement by an order of magnitude.

To further elucidate the role of crystallinity relative to the photomechanical output, the 6FDA/PMDA copolymers with intermediate crystalline contents were examined upon irradiation of 100 mW cm^{-2} of $\lambda = 442$ nm light. As illustrated in the images in Figure 2 a–e, the bending angle decreases as the PMDA concentration is increased from 12.5 mol% (azo-coPI-25) to 37.5 mol% (azo-coPI-75). The importance of sample geometry is also apparent in Figure 2, as increasing the width of the cantilever from 0.5 mm (Figure 1) to 1 mm (Figure 1) increases the bending angle from 26° to 68°. The overall dependence of the photomechanical response (bending angle) on PMDA content for the five polymers examined here is contrasted in Figure 2 with respect to crystallinity as a function of PMDA concentration.

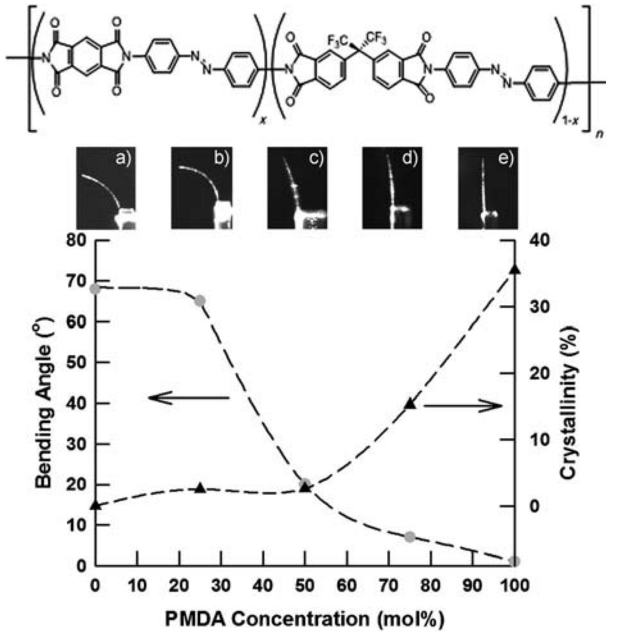

Figure 2. Summary of photomechanical response (bending angle) and crystallinity as a function of PMDA concentration for a series of azobenzene-functionalized linear polyimides (generic structure inset). Images of 5 mm × 1 mm × 0.02 mm cantilevers composed of azo-PI-6FDA (a), copolymers of 6FDA/PMDA (azo-coPI-xx) (b–d), and azo-PI-PMDA (e) after 1 h of irradiation with $\lambda = 442$ nm light polarized parallel to the long axis of the cantilever.

From Figure 2, it is clear that there is a strong relationship between composition, polymer network morphology, and resulting photomechanical response. As evidenced in Figures 1 and 2, cantilevers composed of less than 50 mol% PMDA are amorphous, bend, and can generate a large stress; whereas the cantilevers composed of more than 50 mol% PMDA are semi-crystalline, do not bend, and generate approximately one-third less stress. As discussed previously, the radius of curvature (e.g. the bending angle) of a cantilever is dependent on geometry (width, thickness) and photogenerated strain, and importantly, independent of the modulus of the material system. Thus, the bending cantilever results in Figures 1 and 2 cannot be attributed to the increase in modulus that accompanies the increase in crystallinity. It is clear from Figure 1 c that irradiation of azo-PI-PMDA does yield some response—measureable as stress. Unlike the bending experiments, the stress measurements are coupled to modulus. However, increasing the modulus through increased crystallinity should result in an increase in photogenerated stress. The data in Figure 1 c indicates that in fact the opposite is observed. Thus, it is clear from Figures 1 and 2 that both from the perspective of photogenerated strain and photogenerated stress that increasing crystallinity reduces the ability of the macromolecular system to translate light into work.

The ability of these macromolecular material systems to translate light into work is dependent on the ability of the azobenzene chromophore to isomerize and induce conformational changes, which are manifested as local strains on the chain architecture that are summed and transferred into a macroscopic response. The photoresponsivity of the amorphous azo-PI-6FDA as well as the azo-PI-PMDA material systems were quantified before, during, and after irradiation at $\lambda = 442$ nm as well as at $\lambda = 375$ nm (Figure 3). Note that the molar concentration of azobenzene in the series of polyimides examined here is constant. As apparent in Figure 3 a, the azo-PI-6FDA material has a slight decrease in the trans absorption at $\lambda = 345$ nm over the course of 16 hours of irradiation with $\lambda = 442$ nm. The decrease in trans absorption is accompanied by a slight increase in the cis absorption.[38] Comparatively, the absorbance spectra of azo-PI-PMDA exhibits similar changes over the course of 16 hours of irradiation. To more clearly distinguish the photochemical

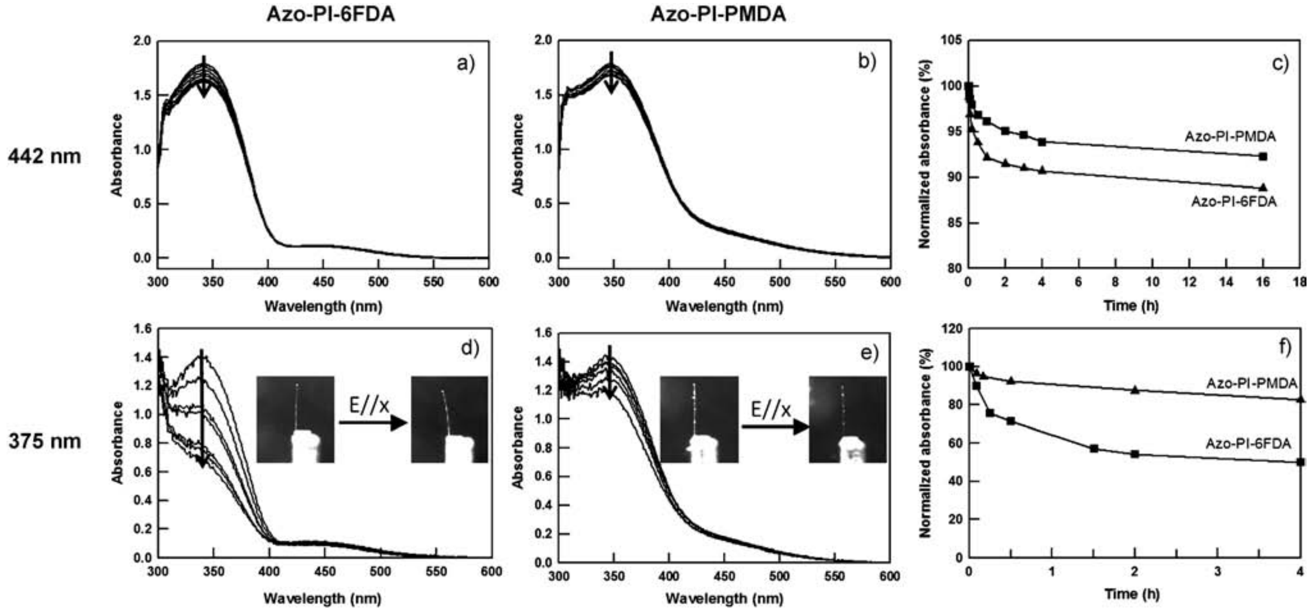

Figure 3. Absorption spectra of azo-PI-6FDA (a) and azo-PI-PMDA (b) during continuous irradiation at 100 $\mathrm{mW\,cm^{-2}}$ of $\lambda = 442$ nm light. c) The peak absorbance of the two materials is plotted as a function of irradiation time. Absorption spectra of azo-PI-6FDA (d) and azo-PI-PMDA (e) during continuous irradiation at 50 $\mathrm{mW\,cm^{-2}}$ of $\lambda = 375$ nm light. f) The peak absorbance of the two materials is plotted as a function of irradiation time.

response of these materials, the peak absorbance is plotted against irradiation time in Figure 3c, and it is clear that azo-PI-6FDA maintains a faster initial photochemical response as well as a larger overall response. To confirm the results in Figures 3a–c, we examined the photochemical response of the materials to UV irradiation—which simply causes trans to cis isomerization of azobenzene. As evidenced in Figures 3d–f, the azo-PI-PMDA sample also exhibits a reduced photochemical response. The photomechanical response of azo-PI-6FDA and azo-PI-PMDA upon irradiation with $\lambda = 375$ nm light are shown as insets in Figures 3d and e. As in Figures 1 and 2, a cantilever composed of azo-PI-6FDA bends upon irradiation while a cantilever composed of azo-PI-PMDA does not.

From Figure 3, it is clear that the amorphous azo-PI-6FDA is capable of faster and larger scale photochemical changes (discernable through changes in the absorption spectra) upon irradiation with both $\lambda = 442$ and 375 nm. It is known[39] that the rigidity of crystalline regions can reduce or even negate the ability of the azobenzene chromophore to isomerize. Similar to these previous reports, we attribute the reduction in the ability to transduce light into mechanical outputs—both strain and stress—to the reduction in photoresponsivity that accompanies the increase in crystallinity in these macromolecular systems. This work is distinct from these prior efforts in that it elucidates the convoluted role of crystallinity in the context of a mechanical system—drawing out the interrelation between local molecular packing (morphology) on the efficacy of photoisomerization (photochemistry) to create useful photomechanical responses (strain or stress). Based on the results presented here, it is expected that the photomechanical response of non-liquid-crystalline photoresponsive macromolecular networks will strongly depend on process history—in particular, local free volume.

In summary, polarization-controlled photodirected bending is observed in azobenzene-functionalized polyimides with T_g values exceeding 350 °C and storage moduli of more than 6 GPa. The photogenerated tensile stress in these materials is as much as an order of magnitude larger than observed in glassy azobenzene-liquid crystalline polymer networks. Through systematic variation of the composition of the linear, main-chain azobenzene-functionalized polyimides, it is shown that crystallinity decreases the magnitude of bending as well as tensile stress. The reduction in photomechanical output with crystalline content is attributed to a reduction in the photoresponsivity of the material system, which was confirmed through spectroscopic examination of the materials before, during, and after irradiation with blue-green and UV light.

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