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# Photomechanical Response of Glassy Azobenzene Polyimide Networks

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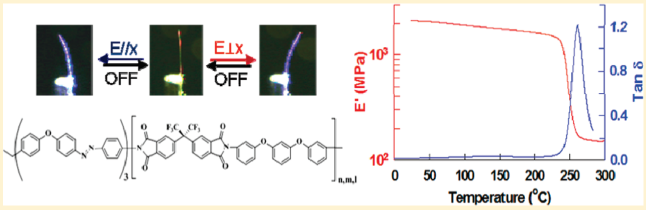
S *Supporting Information*

**ABSTRACT:** We report the synthesis of amorphous, heat-resistant ($T_g$ ranging from 220 to 246 °C) polyimides cross-linked with a novel tris(azobenzeneamine) cross-linker and examine the photodirected bending of cantilevers composed of these materials to exposure to linearly polarized, 442 nm light. Increasing the cross-linker concentration from 5 to 20 mol % in the network not only serves to increase the $T_g$ and modulus but also results in a considerable increase in photomechanical response observed as an increase in bending angle from 5° to 20°. Adjustment of the orientation of the electric field of the light polarization to the cantilever axis is shown to generate forward and backward (bidirectional) bending. Upon removal of the incident light, the cantilevers exhibit photoelastic behavior by restoring to the original vertical position.



## INTRODUCTION

Lovrien postulated in 1967 that light could be transduced into mechanical work in polymeric materials containing photochromic molecules.[1] Eisenbach published a series of work that explored photochromic processes in *bulk polymers* with respect to free volume, detailing reversible photomechanical strain of as much as 0.25%.[2] Building from these ground-breaking contributions, a number of efforts (documented in recent reviews[3]) continue to explore the synthesis of photoresponsive polymers and the characterization of their photomechanical output. Notably, Ikeda et al.[12] demonstrated photodirected, polarization-controlled bending of azobenzene-containing liquid crystalline films. To date, azobenzene has been the most-utilized photochromic unit in the examination of photoresponsive amorphous, crystalline, and liquid crystalline polymers because of its excellent thermal stability, resolved isomeric forms, unique optical nonlinearities, and ability to form birefringent gratings/surface-relief structures when subjected to conventional or polarization holography.[4,5]

The resulting photomechanical output of a polymeric material is dependent not only on its optical properties (absorption wavelength, wavelength of exposure, polarization of exposure) but also on its morphology (amorphous, crystalline, liquid crystalline) and thermomechanical properties. With regard to transducing light into mechanical work, recent efforts have nearly exclusively employed azobenzene-functionalized liquid crystal polymer networks (azo-LCN, both glasses and elastomers). For specific combinations of azo-LCN, sample geometry, and optical excitation, relatively large photomechanical responses have been realized, typified by bending of cantilevers[6−13] or dramatic uniaxial contractions of thin films.[14−16] Exposure to UV light decreases the order of the LC mesogen through trans−cis photoisomerization, at times resulting in an isothermal phase transition. Reverse cis−trans isomerization with subsequent exposure to visible light >530 nm recovers the original molecular alignment, order, and macroscopic shape. Comparatively, the use of visible light (442 or 488 nm) absorbed by both the trans and cis isomeric forms of azobenzene has yielded additional photomechanical responses such as polarization controlled forward and reverse bending of a cantilever.[7,11]

Polyimides (PIs) represent an important class of heat-resistant polymers useful in a variety of applications. The excellent combination of their physical properties, thermal stability, and processability has led to broad application.[17,18] In optical applications, PIs containing main-chain or side-chain azobenzenes, for example, have been investigated for photoinduced alignment in liquid crystal display as well as nonlinear optical (NLO) devices.[19] More recently, an azobenzene-containing poly(amic acid) (a PI precursor) was cross-linked by a triamine in *N*,*N*-dimethylformamide (DMF); the resulting sol−gels showed a 2-fold increase in the storage modulus after irradiation with 405 nm light,[20] and the photomechanical response of a related aromatic poly(amic acid) was reported.[21] While azobenzene-functionalized polyimide films have been extensively employed in a variety of optical applications, the use of these materials for the transduction of light into work, however, is scarce.[4,22]

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In this paper, we report on the large-amplitude, polarization-controlled bidirectional bending of cantilevers composed of new, glassy polyimides containing a novel tris(azobenzeneamine) cross-linker. Here, we describe both the synthesis and the photomechanical response of these materials. The large modulus and glassy nature of these materials distinguish these materials for light-to-work transduction.

## ■ EXPERIMENTAL SECTION

**Materials.** 1,3-Bis(3-aminophenoxy)benzene (BAPB) was (99% min) was purchased from Chriskev Co., Inc., and used as received. All other reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise noted.

**Instrumentation.** The materials were subjected to dynamic mechanical analysis (DMA) in a nitrogen atmosphere with a heating rate of 4 °C/min on TA Instruments DMA Q400EM.

**1,1,1-Tris[4-(4-nitrophenoxy)phenyl]ethane (3).** Into a 250 mL three-necked flask equipped with a magnetic stir bar and nitrogen inlet and outlet were placed 1,1,1-tris(4-hydroxyphenyl)ethane (10.0 g, 33.0 mmol), 1-fluoro-4-nitrobenzene (15.4 g, 109 mmol), potassium carbonate (15.1 g, 109 mmol), and DMF (100 mL). The mixture was stirred at room temperature for 24 h and filtered. The filtrate was diluted with ethyl acetate (400 mL), and the organic layer was separated. The organic layer was washed with water three times. It was dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated to 75 mL on a rotary evaporator and then stored in refrigerator for several days to afford 11.2 g (51%) of off-white crystals, mp 98−99 °C. MS (*m*/*e*): 669 ($M^+$). Anal. Calcd for $C_{38}H_{27}N_3O_9$: C, 68.18%; H, 4.06%; N, 6.27%; O, 21.50%. Found: C, 67.69%; H, 4.26%; N, 6.21%; O, 21.22%. FT-IR (KBr, $cm^{-1}$): 3076, 2979, 1586, 1513, 1486, 1344, 1248, 1165, 1107, 874, 846. $^1$H NMR (DMSO-$d_6$, $\delta$ in ppm): 2.26 (s, 3H, C*H*$_3$), 7.17−7.27 (m, 18H, Ar−*H*), 8.28−8.31 (d, 6H, Ar−*H*).

**1,1,1-Tris[4-(4-aminophenoxy)phenyl]ethane (4).** 1,1,1-Tris[4-(4-nitrophenoxy)phenyl]ethane (**3**; 5.0 g, 7.5 mmol), THF (50 mL), and 5% palladium on activated carbon (0.50 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 55 psi. After the mixture had been agitated at room temperature for 24 h under the hydrogen pressure of 55 psi, it was filtered through Celite. The filter cake was washed with THF, and then the filtrate was evaporated to dryness on a rotary evaporator to afford a 4.25 g (98%) of yellow crystal, which was used without further purification; mp 220−221 °C. MS (*m*/*e*): 579 ($M^+$). Anal. Calcd for $C_{38}H_{33}N_3O_3$: C, 78.73%; H, 5.74%; N, 7.25%. Found: C, 78.17%; H, 5.78%; N, 7.04%. FT-IR (KBr, $cm^{-1}$): 3441, 3361 ($NH_2$), 3035, 2970, 1617, 1581, 1497, 1384, 1232, 1173, 1117, 1010, 871, 842. $^1$H NMR (DMSO-$d_6$, $\delta$ in ppm): 2.02 (s, 3H, C*H*$_3$), 4.99 (s, 6H, N*H*$_2$), 6.53−6.58 (d, 6H, Ar−*H*), 6.68−6.74 (m, 12H, Ar−*H*), 6.88−6.93 (d, 6H, Ar−*H*).

**Synthesis of *N*-(4-Nitrosophenyl)acetamide (5).** After oxone (potassium peroxymonosulfate, from Aldrich; 12.28 g, 20.0 mmol) had dissolved completely in water (100 mL), potassium carbonate (4.14 g, 30 mmol) was added slowly to neutralize the solution to a weak acidity. The solution was added quickly into a solution of 4′-aminoacetanilide (Aldrich; 1.50 g, 10.0 mmol) in water (150 mL). The mixture immediately turned green, and then, greenish-gray solids started to fall out of solution. After the mixture had been stirred for another 10 min, the precipitates were collected on a filter funnel, air-dried, and recrystallized from hot ethanol. Two batches of products isolated as greenish crystals were collected to give a total yield of 1.06 g (65%); mp 179−180 °C (lit.[25] 179−180 °C).

**Synthesis of 1,1,1-Tris{4-[4-(4-acetamidophenyldiazenyl) phenoxy]phenyl}ethane (6).** 1,1,1-Tris(4-(4-aminophenoxy)phenyl)ethane (**4**; 0.580 g, 1.00 mmol), *N*-(4-nitrosophenyl)acetamide (**5**; 0.985 g, 6 mmol), and acetic acid (20 mL) were charged into a 150 mL round-bottomed flask equipped with a magnetic stir bar. The mixture was stirred at room temperature for 48 h. The mixture was at first turned into a greenish solution, and then yellow particles began to precipitate out of the solution. The mixture was diluted by deionized water (100 mL). Solids were collected and washed with water (500 mL) followed by ethanol (200 mL) to remove most of the unreacted nitroso reagent. Then, the solid was extracted by hot acetone (100 mL) four times. The acetone extract was concentrated on a rotary evaporator to give yellow solids as raw product. The raw product was slurried in hot ethanol (50 mL) and filtered after cooled to room temperature twice to give 0.62 g (61%) of yellow solids; mp 220 °C (dec). $^1$H NMR ($d_6$-DMSO, $\delta$ in ppm): 2.09 (s, 9H, COC*H*$_3$), 2.15 (s, 3H, CC*H*$_3$) 7.03−7.15 (m, 18H), 7.79−7.87 (m, 18H) 10.28 (s, 3H, N*H*CO). $^{13}$C NMR ($d_6$-DMSO, $\delta$ in ppm): 24.16, 30.28, 51.00, 118.50, 118.86, 119.18, 123.42, 124.35, 129.99, 142.09, 144.50, 147.38, 147.77, 153.78, 159.07, 168.06.

**Synthesis of 1,1,1-Tris{4-[4-(4-aminophenyldiazenyl)phenoxy]phenyl}ethane (7a).** To a 100 mL round-bottomed flask with a stir bar and a condenser, 1,1,1-tris[4-(4-(4-acetamidophenyldiazenyl)-phenoxy)phenyl] ethane (**6**; 0.50 g, 0.49 mmol), 6 M HCl (20 mL) and 95% ethanol (20 mL) were charged and heated to 80 °C. The mixture was stirred at 80 °C for 3 days. After it was allowed to cool to room temperature, water (60 mL) was added. The resulting red solid was collected by filtration and washed with dilute sodium bicarbonate solution, followed by deionized water (300 mL). After air-dried, the crude product was purified by column chromatography (silica gel, ethyl acetate as eluent). The solvent was removed by a rotary evaporator to afford 0.23 g (52.5%) of orange red solid; mp >300 °C. MS (*m*/*e*): 892 ($M^+$). Anal. Calcd for $C_{56}H_{45}N_9O_3$: C, 75.40%; H, 5.08%; N, 14.13%. Found: C, 75.44%; H, 5.08%; N, 13.98%. $^1$H NMR ($d_6$-DMSO, $\delta$ in ppm): 2.12 (s, 3H, CC*H*$_3$), 6.03(s,6H, N*H*$_2$), 6.67−6.70 (d, 6H, *J* = 8.7 Hz), 6.99−7.02 (d, 6H, *J* = 8.7 Hz), 7.09−7.13 (m, 12H), 7.62−7.66 (d, 6H, *J* = 8.7 Hz), 7.75−7.78 (d, 6H, *J* = 8.7 Hz). $^{13}$C NMR ($d_6$-DMSO, $\delta$ in ppm): 30.34, 51.91, 113.41, 118.44, 118.69, 123.52, 124.96, 129.93, 142.92, 144.25, 148.41, 152.56, 154.21, 157.75.

**Model Compound Synthesis (1,1,1-Tris{4-[4-(4-phthalimidophenyldiazenyl) phenoxy]phenyl}ethane, 7b).** Into a 250 mL three-necked flask equipped with a magnetic stir bar and nitrogen inlet and outlet were placed 1,1,1-tris{4-[4-(4-aminophenyldiazenyl)phenoxy]phenyl}ethane (0.892 g, 1.00 mmol), phthalic anhydride (0.444 g, 3.00 mmol) and acetic acid (20 mL). The mixture was stirred under refluxing 14 h and allowed to cool to room temperature. The precipitate was collected by filtration and dried in oven to afford 0.96 g (75%) of orange powder; mp >300 °C. MS (*m*/*e*): 1282 ($M^+$). Anal. Calcd for $C_{80}H_{51}N_9O_9$: C, 74.93%; H, 4.01%; N, 9.83%. Found: C, 75.00%; H, 4.11%; N, 9.44%. $^1$H NMR ($d_6$-DMSO, $\delta$ in ppm): 2.21 (s, 3H, CC*H*$_3$), 7.08−7.13 (d, 6H, Ar−*H*), 7.19−7.21 (dd, 12H, Ar−*H*), 7.67−7.71 (d, 6H, Ar−*H*), 7.87−8.03 (m, 24H, Ar−*H*).

**Representative Procedure for the Synthesis of Azobenzene-Containing CP2 Polyimides (20 mol %, 12c).** BAPB (0.4093 g, 1.400 mmol) and DMAc (8 mL) were added to a 50 mL three-necked flask equipped with a magnetic stirrer, nitrogen inlet, and outlet and stirred under dry nitrogen at room temperature for 30 min. 6FDA (0.8885, 2.000 mmol) was then introduced to the resulting solution. The light yellow solution was agitated at room temperature for 24 h to afford a poly(amic acid) solution (**10**). Then, the tris(azobenzeneamine) cross-linker (**7a**; 0.3568 g, 0.400 mmol) was added to this solution. After **7a** had completely dissolved in DMAc, the mixture poured into a glass Petri dish, followed by vacuum evaporation of DMAc at 50 °C, and heat-treated according to following schedule: 100 °C/2 h, 150 °C/2 h, 175 °C/1 h, 200 °C/2 h, 250 °C/1 h, and 300 °C/1 h to form polyimide films. The film thickness was ~20 $\mu$m. This procedure was followed to prepare CP2 and its tris(azobenzene)-containing derivatives.

## RESULTS AND DISCUSSION

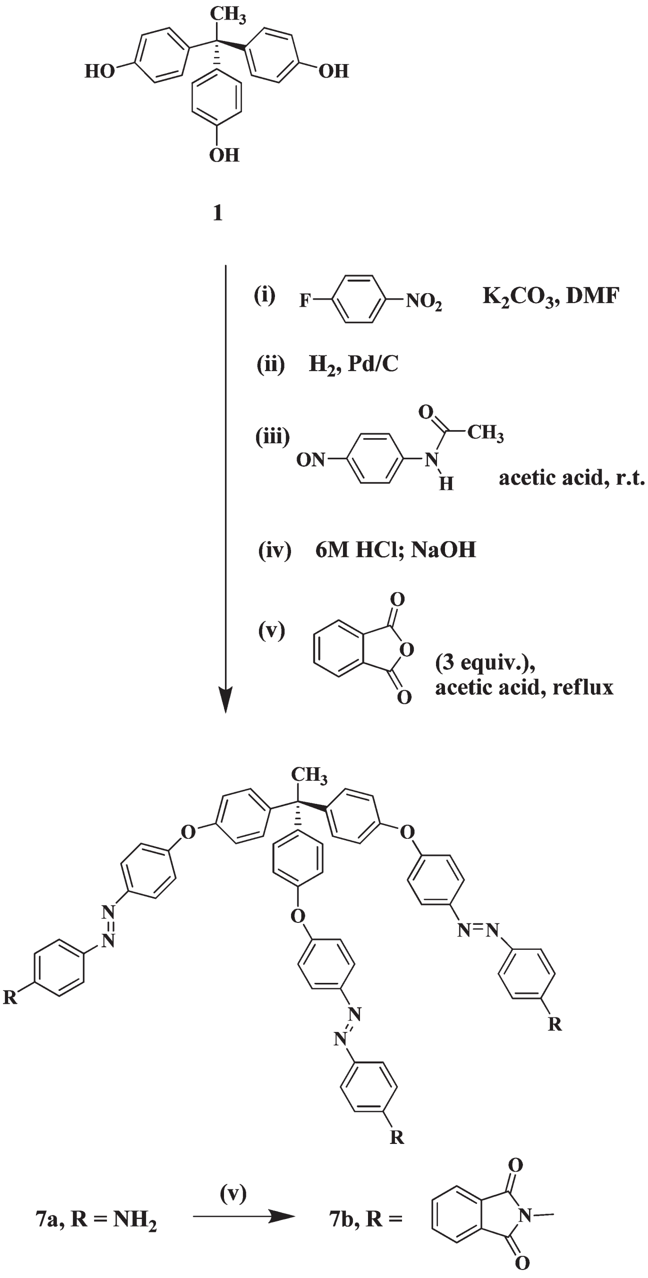
As first postulated by Lovrien, light can be tranduced into mechanical work through conformational changes of photoisomerizable groups bound within the polymer network. Hugel et al. have examined the efficiency of the light-to-work transduction in azobenzene-containing polymers at a molecular level using an atomic force microscope (AFM). Their results indicate that the isomerization process is about 10% efficient; that is, 10% of the incident photon energy ($4 \times 10^{-19}$ J) is converted to mechanical work ($\sim 4.5 \times 10^{-20}$ J).[23] Photomechanical responses at the macroscopic scale, be that in cantilever or film form, are significantly less than 1% efficient to date. As recently shown in liquid crystalline systems,[24] one means to improve the transduction efficiency is through the use of cross-linked azobenzene-actuating units in PI network structure. As such, this work reports the synthesis and photomechanical response of cross-linked, glassy, azobenzene-functionalized polyimides that may show improved light-to-work transduction.

**Cross-Linker Synthesis.** Toward this end, a cross-linking agent was designed to contain three azobenzenes per molecule, viz. tris(azobenzeneamine) monomer (**7a**, Scheme 1), which was then synthesized via a four-step route. To prepare **7a**, 1,1,1-tris(4-hydroxyphenyl)ethane (**1**) was treated with 1-fluoro-4-nitrobenzene (**2**) in the presence of potassium carbonate to yield 1,1,1-tris[4-(4-nitrophenoxy)phenyl]ethane (**3**), which was reduced to 1,1,1-tris[4-(4-aminophenoxy)phenyl]ethane (**4**) by catalytic hydrogenation. The condensation reaction of **4** and 4-nitrosoacetanilide[25] (**5**) in acetic acid yielded **6**, a precursor containing three azobenzene units. The tris(azobenzeneamine) cross-linker (**7a**) was generated after the deprotection of **6** via alkaline deacetylation. End-capping **6** with phthalic anhydride generated the diphthalimidotris(azobenzene) model compound (**7a**).

**UV−vis Spectroscopy of Model Compound.** Reversible trans−cis photoisomerization of the model compound, **7b**, was investigated in THF solution. After irradiation with 366 nm for 10 min, the UV ($\pi \rightarrow \pi^*$) band centered at 383 nm disappears, indicating that all the trans-isomers are converted into cis-isomers. At the same time, the absorbance at 443 nm, which corresponds to cis-isomers, increases to a maximum. In the dark, the cis-isomers undergo thermally activated cis−trans isomerization, and the absorption peak of trans-isomers is totally recovered in 2 days (Supporting Information, Figure S1).

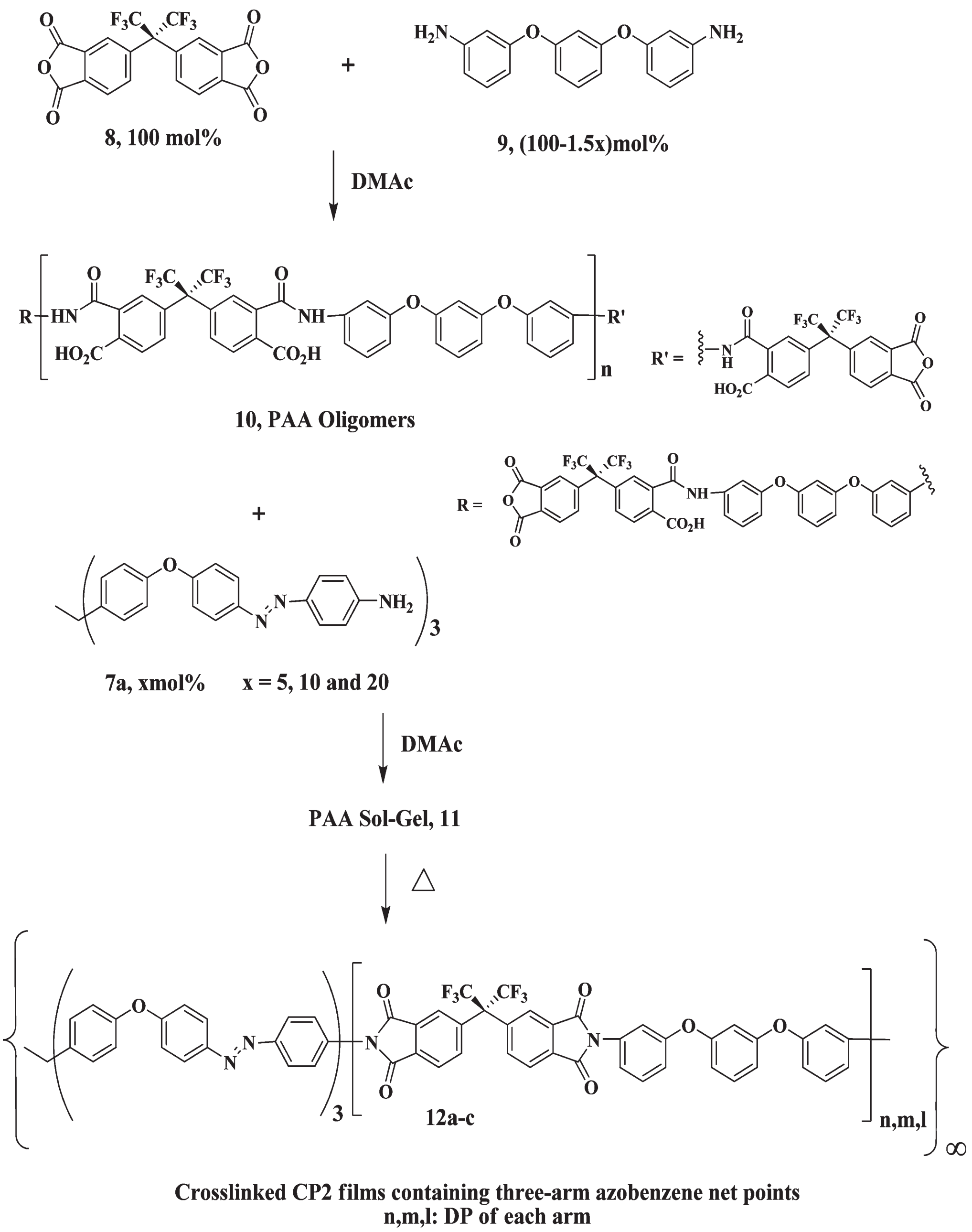
**Azo-CP2 Synthesis.** The polyimide examined here is related to a well-known low-color, space-grade polyimide (CP2)[26,27] derived from 2,2-bis(phthalic anhydride)-1,1,1,3,3,3-hexafluoroisopropane (6-FDA) and 1,3-bis(3-aminophenoxy)benzene (APB). Recently, we have used CP2 as a well-performing matrix for a SWNT nanocomposite electrothermal−actuation system.[28] Scheme 2 outlines the synthesis of azobenzene-containing CP2 (azo-CP2). Briefly, 6-FDA (**8**) and APB (**9**) were dissolved under a nitrogen atmosphere in *N,N*-dimethylacetamide (DMAc) (5 wt % concentration) at room temperature for 24 h with excess 6-FDA to generate poly(amic acid) oligomers (PAA oligomers, **10**) with terminal anhydride groups. Subsequently, the tris(azobenzeneamine) monomer (**7a**) was added to the solution of PAA oligomers with a stoichiometric ratio of the amino group to the terminal acid anhydride. After **7a** had completely dissolved, the resulting PAA sol−gel precursor was poured onto glass slides and cured in an oven set to 300 °C to simultaneously cross-link and imidize the polymer films.

**Scheme 1. Syntheses of Tris(azobenzeneamine) Monomer (7a) and Diphthalimide-End-Capped Model Compound (7b)**



The concentration of azobenzene was varied in the azo-CP2 films by adding specific amounts (i.e., 5, 10, and 20 mol %) of tris(azobenzeneamine) monomer (**7a**) to the respective PAA/DMAc solutions. The molar ratios of the ternary mixtures (6FDA:APB:**7a**) are listed in Table 1. As expected, the cross-linking density increases with an increase in cross-linker concentration, which correspondingly decreases the calculated average molecular weight between cross-links ($M_c$).[29] The glass transition temperature ($T_g$) of the neat polyimide (CP2) is found to be 219 °C by dynamic mechanical analysis (DMA).[30] Comparatively, the $T_g$ values (220−246 °C) of the azobenzene-containing polyimide networks (azo-CP2-*xx*, see Table 1 and Figure S3) increase with the concentration of tris(azobenzene) cross-linker.

**Scheme 2. Synthesis of Azobenzene-Containing CP2 Polyimide Networks, 12a−c**



Polarized optical microscopy (POM) confirms the amorphous nature of the azo-CP2 network (Figure S4).

The tensile moduli (*E*) of the azo-CP2 films initially decrease with the presence of cross-linker (0−5 mol %) as compared to that of neat CP2 before subsequently increasing by ~0.2 GPa per 5 mol % of cross-linker added. It is speculated that at cross-linker concentrations ≤5 mol %, the tripod geometry of the cross-linker may be disrupting the chain-packing regularity of the CP2 polyimide, resulting in softening of the azo-CP2 networks. However, further increasing cross-link density (correspondingly decreasing $M_c$ between the net points) in the azo-CP2 systems results in the expected increase in modulus with each addition of 5 mol % cross-linker.

**Photomechanical Behavior.** The photomechanical response of cantilevers composed of azo-CP2-20 is depicted in Figure 1, which plots the magnitude of bending angle against polarization angle to uniform exposure to a linearly polarized blue laser of (442 nm in wavelength) with an intensity of 120 mW/cm$^2$. Note that the direction of the laser exposure in the images presented here is from left to right. Interestingly, despite the glassy nature of the azo-CP2-20 network, the cantilever bends more than 20° when exposed to the light polarized parallel to the long axis ($E \parallel x$, 0°) of the cantilever. As polarization angle is shifted from 0° to 15°, the magnitude of bending decreases. When the polarization of the laser is 45° to the long axis of the cantilever, no bending is observed. At polarization angles greater than 45°, bending occurs in the reverse direction with greatest magnitude when the azo-CP2-20 cantilever is exposed to light polarized orthogonal to the long axis ($E \perp x$, 90°) of the cantilever. The forward and reverse bending directions are uniform and symmetrical. As evident in

Table 1. Composition and Properties of Polyimide Films

| sample | 6FDA (mol %) | BAPB (mol %) | **7a** (mol %) | $T_g^b$ (°C) | $E^c$ (GPa) | $M_c$ (Da) | $\alpha_{442}^d$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| CP2 | 100 | 100 | 0 | 219 | 1.9 ± 0.15 | | |
| azo-CP2-05 (**12a**)[a] | 100 | 92.5 | 5 | 220 | 1.6 ± 0.2 | 7241 | 379 |
| azo-CP2-10 (**12b**)[a] | 100 | 85 | 10 | 226 | 1.8 ± 0.2 | 4317 | 470 |
| azo-CP2-20 (**12c**)[a] | 100 | 70 | 20 | 246 | 2.4 ± 0.3 | 2576 | 563 |

[a] The measured thickness of the azo-CP2 films are 18 $\mu$m (azo-CP2-05), 21 $\mu$m (azo-CP2-10), and 21 $\mu$m (azo-CP2-20). The cantilever was uniform in thickness with variation less than 0.5 $\mu$m. [b] $T_g$ measured from the peak of tan delta (DMA) as an average value taken from four measurements. [c] Modulus determined in tension at 25 °C as average from five specimens per sample. [d] Measured absorption coefficient for the materials at 442 nm.

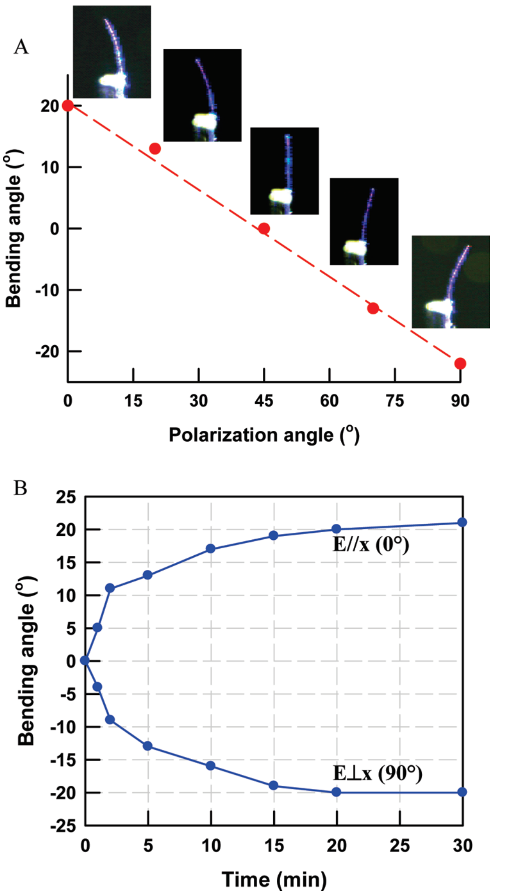


**Figure 1.** Bending angle as a function of (A) polarization angle (angle between polarization direction of linearly polarized light and long axis of cantilever) and (B) time for a cantilever composed of azo-CP2-20 to exposure to a 120 mW/cm$^2$ 442 nm irradiation.

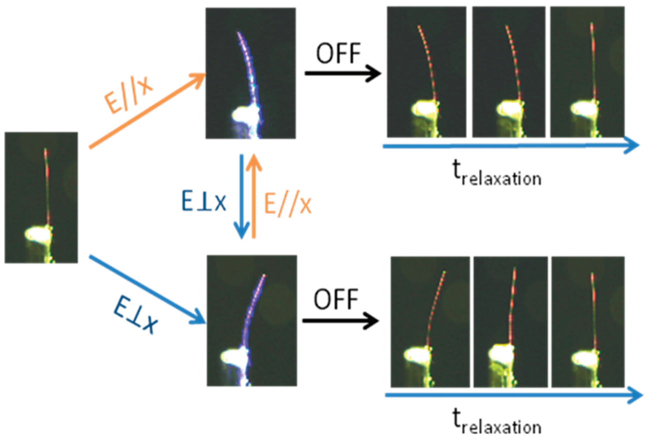


**Figure 2.** Shape-relaxing (photoelastic) of azo-CP2-20 after removal of 442 nm light at irradiance of 120 mW/cm$^2$.

Figure 1, exposure to the 442 nm laser allows for polarization-controlled, reversible forward and backward motions, allowing for remote and precise control of the cantilever displacement.

As discussed in greater detail elsewhere,[9−11] we propose that linearly polarized blue-green (440−510 nm) light induces what has been referred to as trans−cis−trans reorientation (also known as the Weigert effect).[5] This phenomenon has been extensively employed in glassy azobenzene polymers to form both conventional volume gratings and surface relief gratings.[3−5] Fundamental to this mechanism is the simultaneous and repeated trans−cis and cis−trans isomerization cycles of azobenzene induced by light in this wavelength regime. The repeated trans−cis and cis−trans isomerizations of azobenzene, due to the dichroic absorption of azobenzene (in addition to the rotational freedom of the azo bond when photoexcited), result in a statistical buildup of *trans*-azobenzene rotated orthogonal to the incident linear polarization of the light source. Because of the large absorption coefficient of azo-CP2-20 at 442 nm (Table 1), light is absorbed nonuniformly across the thickness of the film. When light is polarized parallel to the long axis of the cantilever, the reorientation of azobenzene results in a contraction along the long axis, which causes bending toward the laser source. Conversely, when light is polarized orthogonal to the long axis of the cantilever, the reorientation of azobenzene causes an expansion along the long axis, which yields bending away from the laser source. The fact that bending is not observed to light polarized 45° to the long axis indicates that the mechanism is not photothermal in nature and is the expected result of a reorientation mechanism. Preliminary calculations indicate that only a small percentage of the azobenzene mesogens need to rotate to generate the strain necessary to drive bending of this magnitude in this glassy system. It is important to note that the magnitude of bend angle is strongly correlated to the aspect ratio of the cantilever and intensity of the illumination.

Figure 2 summarizes the response of azo-CP2-20 after removal of the incident light source. Upon removal of the 442 nm illumination, the cantilever reversibly recovers its original shape within ∼10 min. The deformation/recovery cycle can be repeated hundreds of cycles. In nearly all previous examinations of azo-functionalized glassy liquid crystalline or amorphous polymers, "photoplastic" responses have been observed, evident in

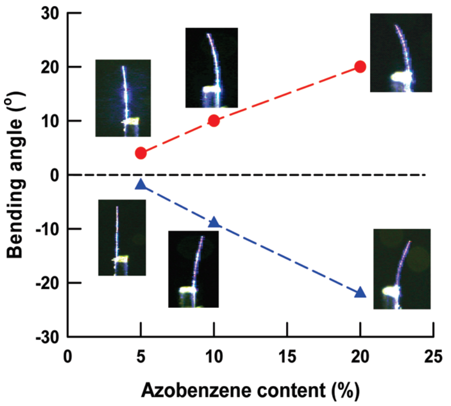


**Figure 3.** Photodirected bending of azo-CP2 cantilevers composed with increasing concentration of azobenzene (5−20 mol %) with the exposure to $E \parallel x$ (●) and $E \perp x$ (▲) of 442 nm laser at 120 mW/cm$^2$.

long-term retention of the grating structure[4] or photomechanical displacement.[10,11] As such, the "photoelastic" relaxation of the bent cantilever to the original vertical position is fairly surprising. For comparison, prior examinations of glassy polydomain azobenzene LCN when exposed to 120 mW/cm$^2$ 442 nm light exhibit a slightly larger bending magnitude and identical polarization dependence but show "photoplastic" shape retention over an extended (months) period of time.[11] The photoelastic response of azo-CP2 is indicative of the nature and extent of photoinduced changes to the network morphology and the subject of future study.

The impact azo-CP2 composition on the magnitude of the photomechanical response is examined by decreasing the concentration of the tris(azobenzeneamine) monomer. Figure 3 plots the maximum bending angle as a function of azobenzene concentration for exposure of cantilevers to a 120 mW/cm$^2$, 442 nm laser, polarized parallel ($E \parallel x$) or orthogonal ($E \perp x$) to the long axis of the cantilever. Reversible bidirectional bending is observed for all three samples with the magnitude of bending angle increasing with increasing tris(azobenzeneamine) monomer concentration. As evident from Table 1, the increase in azobenzene concentration not only influences the optical properties of the films (an increase in absorption coefficient) but also increases the cross-link density (as indicated by the decrease in the average molecular weight of linear segment or $M_c$[27]) and $T_g$ of azo-CP2 networks. Both of these factors are known to strongly influence the resulting photomechanical outcome in analogous glassy azo-LCN.[11]

The large magnitude displacement of these glassy azo-CP2 polyimides may be quite surprising to some, given that these photomechanical deformations are observed nearly 200 °C below the $T_g$ of the polymer. However, the photodirected responses observed in these newly synthesized azo-functionalized glassy polyimides do have some precedent. Agolini and Gay report small photomechanical (contractile) effect based on the stress response at constant length on exposure to a low-power mercury lamp for an aromatic, semicrystalline polyimide (derived from 4,4′-diaminobenzene and pyromellitic dianhydride).[22a] Further, as detailed in the excellent reviews of Tripathy[5] and Barrett,[3c] as well as the recent monograph from Ikeda and Zhao,[3b] photoinduced, cooperative motion has been widely observed in glassy azo-functionalized polymers to form both conventional and surface relief gratings when these materials are subjected to irradiation of similar wavelength to that employed here.

## CONCLUSIONS

In summary, a trifunctional azobenzene cross-linker was synthesized to yield a highly concentrated, azo-functionalized polyimide. The photoresponse of cantilevers composed of the polyimide (azo-CP2) examined here is typified by large magnitude bending, bidirectionality, and photoelastic response to exposure to linearly polarized 442 nm light. The high glass transition temperature, thermal stability, and modulus of these materials allow for potential utility in extreme, high-temperature environments and may increase the likelihood of accomplishing useful work.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Supporting experimental information (Figures S1−S4) depicting UV-vis spectra, DMA results, and polarized optical micrograph. This material is available free of charge via the Internet at http://pubs.acs.org.

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