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**PHOTOPIEZOELECTRIC COMPOSITES OF  
AZOBENZENE-FUNCTIONALIZED POLYIMIDES AND  
POLYVINYLIDENE FLUORIDE (POSTPRINT)**

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# REPORT DOCUMENTATION PAGE

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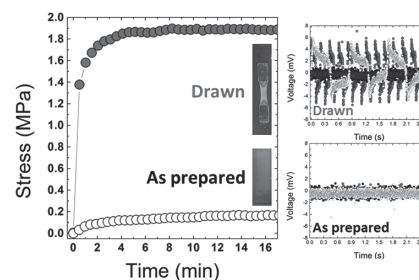
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# Photopiezoelectric Composites of Azobenzene-Functionalized Polyimides and Polyvinylidene Fluoride

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Light is a readily available and sustainable energy source. Transduction of light into mechanical work or electricity in functional materials, composites, or systems has other potential advantages derived from the ability to remotely, spatially, and temporally control triggering by light. Toward this end, this work examines photoinduced piezoelectric (photopiezoelectric) effects in laminate composites prepared from photoresponsive polymeric materials and the piezoelectric polymer polyvinylidene fluoride (PVDF). In the geometry studied here, photopiezoelectric conversion is shown to strongly depend on the photomechanical properties inherent to the azobenzene-functionalized polyimides. Based on prior examinations of photomechanical effects in azobenzene-functionalized polyimides, this investigation focuses on amorphous materials and systematically varies the concentration of azobenzene in the copolymers. The baseline photomechanical response of the set of polyimides is characterized in cantilever deflection experiments. To improve the photomechanical response of the materials and enhance the electrical conversion, the polyimides are drawn to increase the magnitude of the deflection as well as photogenerated stress. In laminate composites, the photomechanical response of the materials in sequenced light exposure is shown to transduce light energy into electrical energy. The frequency of the photopiezoelectric response of the composite can match the frequency of the sequenced light exposing the films.



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## 1. Introduction

Transducing solar energy into electricity has potential benefits both from the perspective of cost savings and environmental sustainability. The marketplace for solar energy harvesting devices is highly competitive and focused on semiconductor-based solar panels. Harvesting approaches conducive to integration on flexible substrates or other complex geometries can tradeoff efficiency for functional benefits as well as cost.<sup>[1,2]</sup> It is within this vein that we investigate a flexible and lightweight approach to light harvesting based on laminate composites of azobenzene-functionalized polyimides (azo-PIs) and the piezoelectric polymer polyvinylidene fluoride (PVDF). The large

piezoelectricity of PVDF via electret formation was first reported by Kawai in 1969.<sup>[3]</sup> PVDF is a dielectric material capable of generating electric current, when the material is subjected to external mechanical force. The applied force induces development of separated positive and negative charges on the material surface.<sup>[4]</sup> In the case of PVDF, the nonpolar  $\alpha$  phase (trans-gauche conformation) has the lowest energy conformation. Under mechanical load, PVDF takes on a zigzag conformation (all-trans) (referred to as the polar  $\beta$  phase), where dipoles are aligned.<sup>[5,6]</sup> This stress-induced adjustment of the chain configuration of PVDF generates electric current and referred to as the “direct” piezoelectric effect. Conversely, employing an electric field to induce a strain response is known as the “inverse” piezoelectric effect.<sup>[5]</sup> Here, we employ PVDF to generate electricity through the direct piezoelectric effect.<sup>[7]</sup>

Compared with studies of the piezoelectric effect,<sup>[8]</sup> photomechanical shape adaptivity is a relatively new concept with less than 50 years of examination.<sup>[9]</sup> A few recent reports detail the transduction of photomechanical response of materials into electrical energy.<sup>[10,11]</sup> For direct conversion of light into mechanical work, photoactive chromophores are often incorporated into cross-linked liquid crystal polymers.<sup>[12–18]</sup> Systematic study of the effects of azobenzene concentration on photomechanical outputs has been performed in liquid crystalline polymer networks (LCNs).<sup>[19]</sup> In azobenzene-based materials, the rod-like trans-azobenzene is isomerized to the bent cis form with UV exposure, which can cause the loss of order particularly in elastomeric LCN materials. Irradiation of azobenzene-based polymeric materials with linearly polarized UV light has been shown to direct the axis of the contraction of the film surface (and bending) in thick specimens.<sup>[12]</sup> Recently, we have reported on the synthesis of azo-PIs and their photomechanical response to the actinic visible light having wavelength of 442 or 445 nm. Compared with UV irradiation, blue light (442 or 445 nm) is nearly equally absorbed by both the trans and cis isomeric forms of the conventional azobenzene chromophore. Accordingly, due to the dichroic absorbance of these isomeric forms, exposing the materials to linearly polarized blue light directs reorientation of the chromophores which resultantly generates either contractile or expansive strains, which have been shown to dictate the directionality (forward or reverse) of a cantilever bending.<sup>[20]</sup>

In our recent examinations of azo-PIs,<sup>[21,22]</sup> structure–property relationships have been developed to correlate the roles of crystallinity,<sup>[22]</sup> free volume,<sup>[23]</sup> alignment,<sup>[24]</sup> backbone rigidity,<sup>[25]</sup> and sub- $T_g$  transitions<sup>[21]</sup> to photomechanical effects observed as bending in cantilevers and quantified stress in tensile testing. Of particular relevance to the work presented here, crystallinity was deleterious to photoresponsiveness as well as strain response.<sup>[22]</sup>

Hence, amorphous 6FDA-based PIs are the focus of this work. Furthermore, we recently reported a markedly different photomechanical response by substitution of dianhydrides in the polymer backbone<sup>[25]</sup> and by a uniaxial chain alignment via hot-drawing.<sup>[24]</sup> By employing a comparatively “soft” dianhydride precursor as well as subjecting the material to processing (hot-drawing), the photomechanical response is large enough such that upon irradiation, time-sequenced photopiezoelectrical energy conversion is realized.

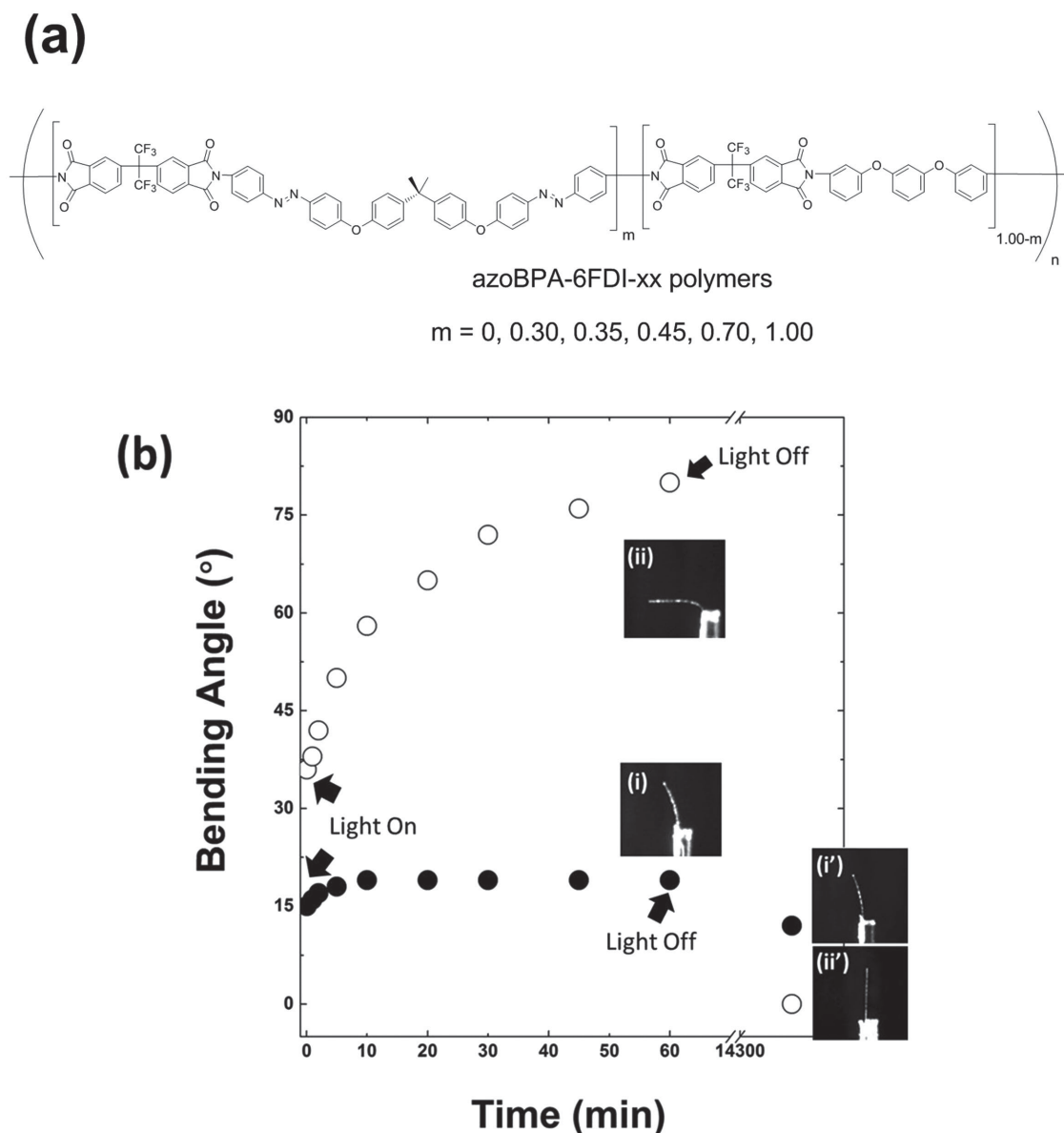
## 2. Experimental Section

### 2.1. General Synthetic Procedure

The 6FDA-based azobenzene-functionalized polyimides were synthesized using 6FDA (1,1,1,3,3,3-hexafluoro-2,2-bis(4-phthalic anhydride)-propane, Akron Polymer Systems), azoBPA (2,2-bis{4-[4-(4-aminophenyldiazenyl)phenoxy]phenyl}-propane), and APB (1,3-bis(3-aminophenoxy)benzene; Chriskev Company). AzoBPA is a diamine containing two azobenzenes per molecule and synthesized according to our previous publication.<sup>[25]</sup> The generic chemical structure shown in Figure 1a for the AzoBPA-6FPI-m series is an idealized representation of the polyimides from the (co)polymerization (see Scheme S1, Supporting Information) of azoBPA (molar fraction = m) and APB (molar fraction = 1.00-m) with 6FDA (molar fraction = 1.00). The experimental details are provided in the Supporting Information. Briefly, 6FDA, azoBPA, and APB were dissolved under nitrogen atmosphere in *N,N*-dimethylacetamide (DMAc) at room temperature for 24 h to generate the corresponding poly(amic acid) precursor (PAA). The PAA precursor solution was poured onto glass slides and cured in an oven at 300 °C to result in the imidized polymer film. The AzoBPA-6FDI homopolymer (i.e., AzoBPA-6FDI-100) was prepared from 6FDA and azoBPA in 1:1 molar ratio, once again using the procedure reported previously.<sup>[25]</sup> The concentration of azobenzene in AzoBPA-6FDI-m copolymers was systematically varied in the azoBPA-6FDI copolymers with respect to the amounts of azoBPA monomer (i.e.,  $m \times 100\%$  or  $xx = 30, 35, 45,$  and  $70 \text{ mol}\%$ ) used in preparing the respective PAA/DMAc solutions. The molar ratios of the ternary mixtures (6FDA:APB:azoBPA) in the azoBPA-6FDI-xx synthesis are listed in Table 1.

### 2.2. Characterization

The thermomechanical properties of the azoBPA-6FDI-xx polymers were investigated by a stress-controlled dynamic mechanical analysis (DMA, TA Instruments, DMA Q800) in a nitrogen atmosphere with a 4 °C min<sup>-1</sup> heating rate. Thermogravimetric analysis (TGA) was conducted in either nitrogen (N<sub>2</sub>) or air atmosphere at a heating rate of 10 °C min<sup>-1</sup> using a TA Hi-Res TGA 2950 thermogravimetric analyzer. Results are summarized in Table 1, Table S1, and Figure S4 (Supporting Information). Wide angle X-ray scattering (WAXS) experiments were carried out by a Rigaku Ultrax18 system with a Statton box camera at 53 mm sample to image plate distances in transmission mode using CuK $\alpha$ .



**Figure 1.** a) Generalized chemical structure of azoBPA-6FDI polymers with  $n$  degree of polymerization. The mole fraction ( $m$ ) of azoBPA-6FDI as expressed in percentage ( $xx$ ) varied from 0%, 30%, 35%, 45%, 70%, and 100%. b) Time-resolved measurements of photomechanical strain responses of 6FDA-coPIs visualized in cantilever bending experiments upon exposure to linearly polarized ( $E||x$ ) 445 nm light at  $120 \text{ mW cm}^{-2}$  for 1 h. Inset images are taken after 1 h of irradiation for (i) azoBPA-6FDI-30 (●) and (ii) azoBPA-6FDI-100 (○). Images marked with apostrophe are taken after 10 d relaxation at dark.

The photomechanical responses of the azoBPA-6FDI polymers were monitored upon exposure to  $120 \text{ mW cm}^{-2}$  of linearly polarized 445 nm light at ambient condition. The orientation of the linear polarization to the sample was adjusted with a Fresnel rhomb (Newport). The cantilever geometry (6 mm ( $L$ )  $\times$  0.1 mm ( $W$ )  $\times$  0.02 mm ( $T$ )) visualizes the strain response of the materials. The bending angle was measured as the angle between the base of the cantilever and the edge of the bent tip. Bidirectional bending behavior was examined using the light-polarized parallel ( $E||x$ ) and perpendicular ( $E\perp x$ ) to the long axis of the cantilever, although only the response to  $E||x$  is reported here.

Hot-drawing of the materials as well as photogenerated stress measurements of azo-PIs were carried out by a strain-controlled DMA (TA Instruments RSA III). Before drawing, the polyimide films were heated to a rubbery state at temperatures of ( $T_g + 70 \text{ }^\circ\text{C}$ ) and equilibrated for 5 min. In a transient mode, azo-PIs films were stretched to draw ratio ( $\lambda = L/L_0$ ) of 3 with a  $0.1 \text{ s}^{-1}$  Hencky strain (or true strain) rate and subsequently air-cooled to ambient condition. Photogenerated stress of both undrawn and drawn azo-PI materials (3 mm ( $W$ )  $\times$  6 mm ( $L$ )  $\times$  0.2 mm ( $T$ )) was measured upon illumination with  $60 \text{ mW cm}^{-2}$  linearly polarized ( $E||x$ ) 445 nm light produced by a light-emitting diode (LED), while the films were held in the DMA at minimal prestrain.



■ **Table 1.** Composition, optical, thermomechanical, and photomechanical properties of the azoBPA-6FDI copolymers.

Sample	Repeat unit chemical formula	azoBPA [mol%]	APB [mol%]	Repeat unit MW [g mol <sup>-1</sup> ]	Chromophore number density [x 10 <sup>20</sup> /cm <sup>3</sup> ]	$\alpha_{445}^a$ [cm <sup>-1</sup> ]	$T_g^b$ [°C]	$E^c$ [GPa]	$\Theta_{1h}^d$ [°]	$\Theta_{dark}^e$ [°]
azoBPA-6FDI-0	C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub>	0	100	700.53	0.00	–	219	1.90 ± 0.15	–	–
azoBPA-6FDI-30	(C <sub>58</sub> H <sub>36</sub> F <sub>6</sub> N <sub>6</sub> O <sub>6</sub> ) <sub>0.30</sub> (C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>0.70</sub>	30	70	798.45	1.47	324 ± 6	237	1.74 ± 0.21	19	14
azoBPA-6FDI-35	(C <sub>58</sub> H <sub>36</sub> F <sub>6</sub> N <sub>6</sub> O <sub>6</sub> ) <sub>0.35</sub> (C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>0.65</sub>	35	65	814.77	1.63	448 ± 15	243	1.57 ± 0.12	45	42
azoBPA-6FDI-45	(C <sub>58</sub> H <sub>36</sub> F <sub>6</sub> N <sub>6</sub> O <sub>6</sub> ) <sub>0.45</sub> (C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>0.55</sub>	45	55	847.41	1.93	578 ± 21	248	1.48 ± 0.10	54	37
azoBPA-6FDI-70	(C <sub>58</sub> H <sub>36</sub> F <sub>6</sub> N <sub>6</sub> O <sub>6</sub> ) <sub>0.70</sub> (C <sub>37</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>0.30</sub>	70	30	929.01	2.45	668 ± 4	269	1.35 ± 0.09	60	0
azoBPA-6FDI-100	C <sub>58</sub> H <sub>36</sub> F <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	100	0	1026.93	2.79	723 ± 13	284	1.10 ± 0.26	80	0

<sup>a</sup>) Experimentally measured absorption coefficient for azoBPA-6FDI copolymers at 445 nm; <sup>b</sup>)  $T_g$  measured from the peak of tan delta; <sup>c</sup>) Modulus (E) is reported from storage modulus (E') values measured with 1 Hz frequency at 25 °C. Error bars are reported from sample to sample variations from five specimens; <sup>d</sup>) Bending angle of azoBPA-6FDI copolymers near an equilibrium photostationary state after irradiation with linearly polarized (E//x) 445 nm light for 1 h; <sup>e</sup>) Bending angle of azoBPA-6FDI copolymers after relaxation in the absence of light for 10 d.

Photoinduced electric current generated from the piezoelectric polymer PVDF was measured by a Tektronix oscilloscope (TDS 3014). One edge of the photoresponsive polyimide film (3 mm (W) × 6 mm (L) × 0.2 mm (T)) is attached to a Au-coated PVDF film (4 cm (L) × 2.5 cm (W) × 8 μm (T) (illustrated in Figure 2a)). To avoid residual piezoelectric signal from photoinduced effects within PVDF, the PVDF was coated with an absorbing layer. Photomechanical deformation of polyimide cantilever was initiated with sequenced irradiation of 270 mW cm<sup>-2</sup> linearly polarized (E//x) 445 nm light at 1.2 or 5 Hz frequency by using a rotating beam chopper.

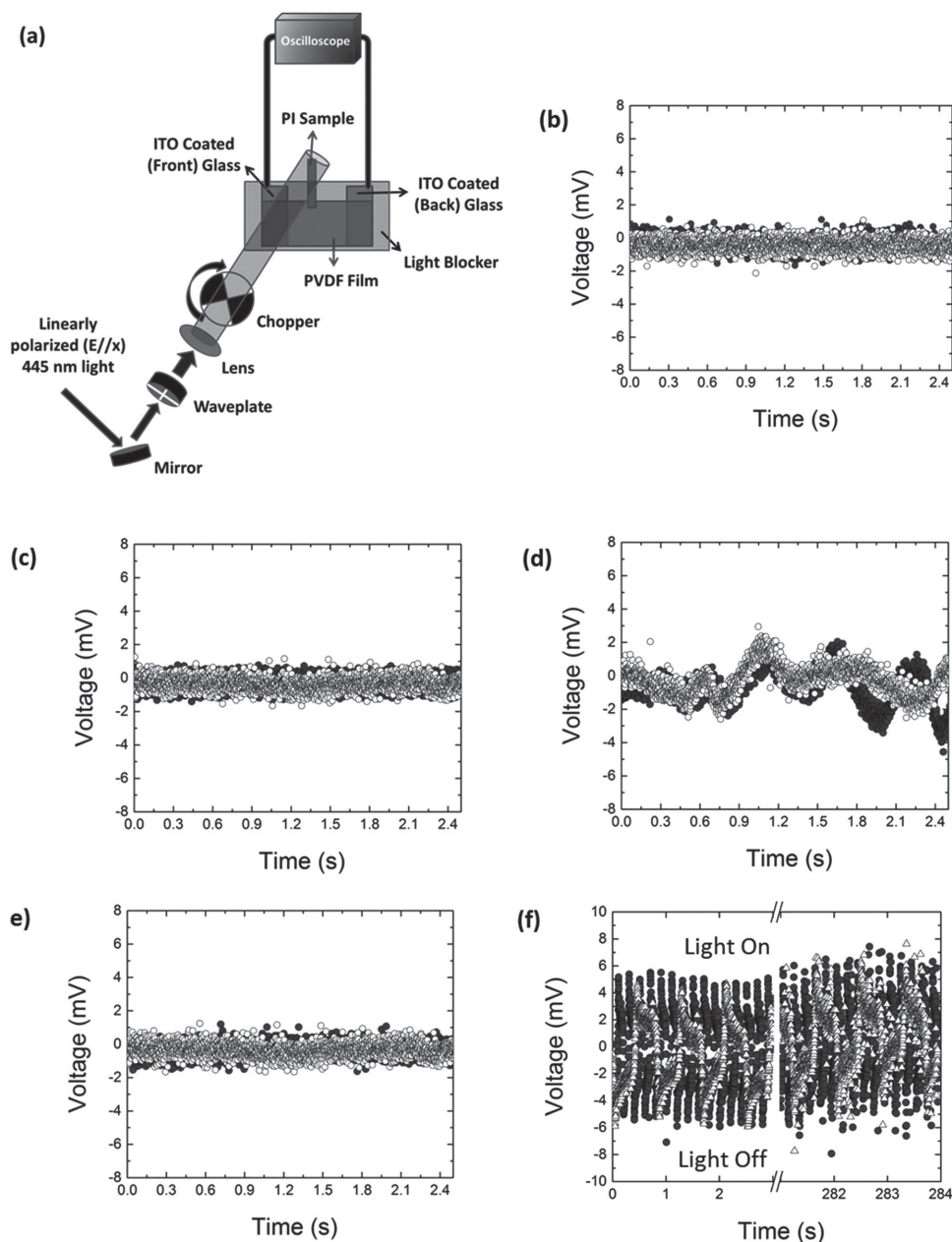
### 3. Results and Discussion

The goal of this effort is to employ the photomechanical response of azobenzene-functionalized polyimides to subject a piezoelectric material (PVDF) to striction to generate electric current (photopiezoelectric effect). Accordingly, we prepared a series of azoBPA-6FDI polymers over a range of azobenzene concentrations. The fundamental properties of the materials are summarized in Table 1. All the polyimides in the series are amorphous and exhibit the expected trend in absorption (as evident in the calculated chromophore number density (CND) as well as the measured absorption coefficient ( $\alpha$ ) over the range of azobenzene concentrations). To visualize the photomechanical response of these materials, the deflection of cantilevers to irradiation with

120 mW cm<sup>-2</sup> of linearly polarized 445 nm light was monitored over the course of 1 h. The maximum equilibrium bending angle for the entire series of azoBPA-6FDI materials is summarized in Table 1. As expected, increasing the azobenzene concentration increases the angle of the deflection in the materials. Furthermore, as evident in Figure 1b, the temporal response of azoBPA-6FDI-100 is comparatively faster than azoBPA-6FDI-30. It is expected that in the generation of electricity by time-sequenced irradiation, the relaxation of the materials will be critical. Inset into Figure 1b (and summarized as  $\Theta_{dark}$  in Table 1), the dark relaxation of the series of azoBPA-6FDI materials are substantially different. From Figure 1b, it is clear that after storage in the dark for 10 d, azoBPA-6FDI-100 relaxes to the original flat shape, whereas azoBPA-6FDI-30 retains a large portion of the deformation. We believe that the wide variance in dark relaxation is attributable to the differences in the modulus as well as the free volume of the materials, which limit the degree of reorientation of the azobenzene chromophores and the ability for the polymer network to retain the distorted chain configuration.

Photopiezoelectric effects were examined in laminates of either azoBPA-6FDI-100 or azoBPA-6FDI-30 and PVDF. The azoBPA-6FDI materials were attached to PVDF in cantilever geometry as illustrated in Figure 2a. The output electric current was measured by an oscilloscope with a 10-MΩ input resistance. The samples were irradiated with a 445-nm laser passing through a beam chopper operating at either 1.2 or 5 Hz. The samples were preexposed



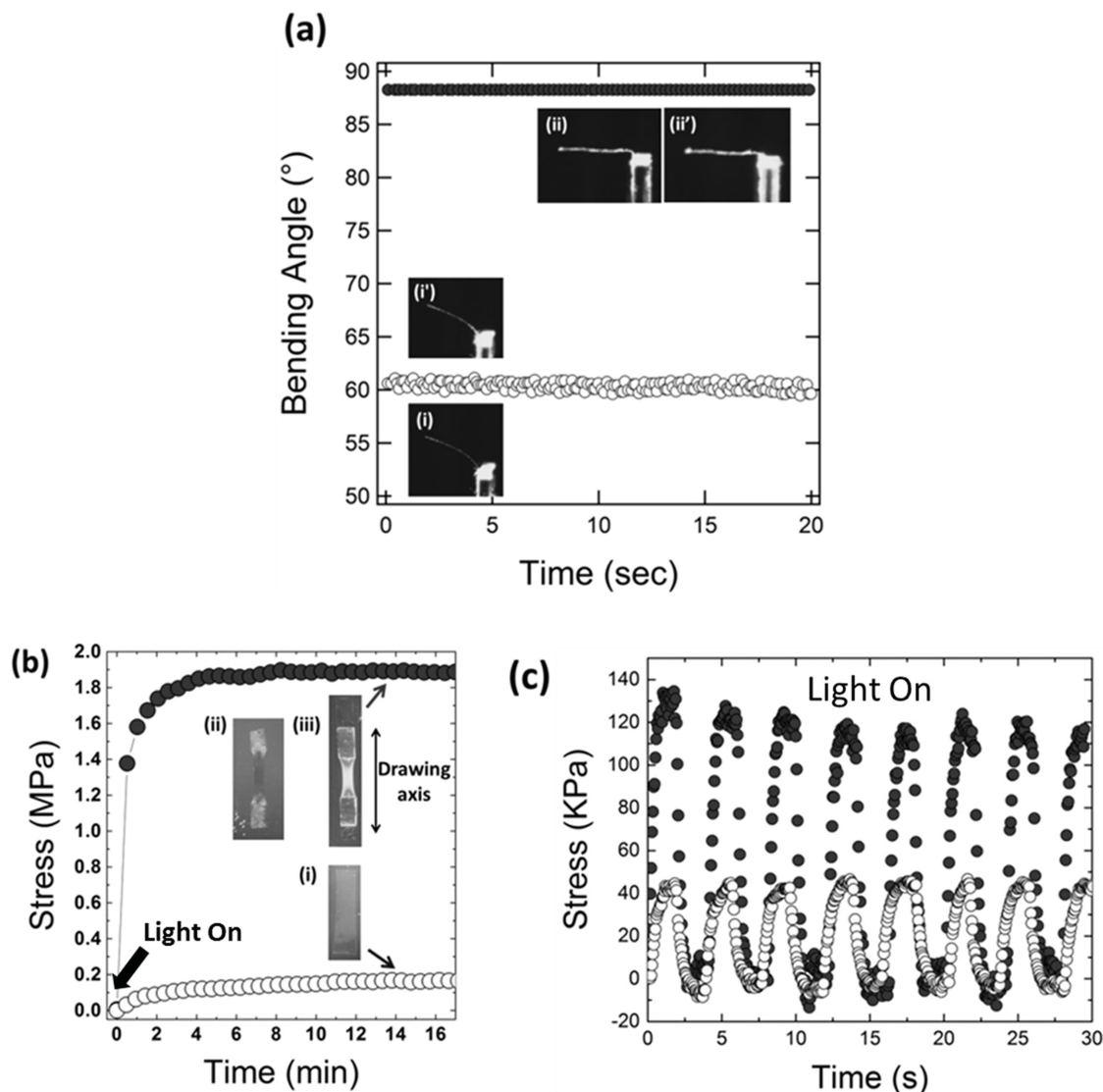


**Figure 2.** a) Illustration of the experimental setup for photopiezoelectricity generation in laminates composed of azoBPA-6FDI polymers and PVDF. In b–f), the polyimide materials were irradiated with  $270 \text{ mW cm}^{-2}$  of linearly polarized ( $E \parallel x$ ) 445 nm light sequenced at 1.2 Hz ( $\circ$ ) or 5 Hz ( $\bullet$ ) through a beam chopper. The voltage was monitored as a function of irradiation time for (b) PVDF, (c) undrawn azoBPA-6FDI-30, (d) drawn azoBPA-6FDI-30, (e) undrawn azoBPA-6FDI-100, and (f) drawn azoBPA-6FDI-100.

for 1 h to allow the system to reach a photostationary state equilibrium. Direct irradiation of PVDF coated with an absorbing layer in the conditions of this examination does not generate electric current (Figure 2b). Irradiation of laminates of PVDF and azoBPA-6FDI-30 or azoBPA-6FDI-100 also generates negligible electric current (Figure 2c,e), regardless of light frequency. However, when the materials are aligned by hot-drawing<sup>[24]</sup> (draw ratio of 3), a measurable electric current is observed in

both materials. In the case of drawn azoBPA-6FDI-30 (Figure 2d), the output frequency of the electric current is irregular and does not match the input light frequency. In contrast, the drawn azoBPA-6FDI-100 laminate generated ca. 4–6 mV output voltage that mirrors the frequency of the incident light sequence.

To further elucidate the fundamental cause of the photoinduced piezoelectricity observed in Figure 2, photoinduced strain and stress responses of



**Figure 3.** Photogenerated strain and stress responses of undrawn (○) and drawn (●) azoBPA-6FDI-100. a) After reaching a photostationary state (after 1 h of preexposure), the films were subjected to sequenced linearly polarized ( $E||x$ ) 445 nm light at 1.2 Hz. Inset images are taken from the side (i) undrawn azoBPA-6FDI-100 in dark, (ii) drawn azoBPA-6FDI-100 in dark, (i') undrawn azoBPA-6FDI-100 during irradiation, and (ii') drawn azoBPA-6FDI-100 during irradiation. b) Temporal evolution of photogenerated stress. Inset images are taken between crossed polarizers for (i) undrawn azoBPA-6FDI-100, (ii) drawn azoBPA-6FDI-100 aligned  $0^\circ$  to the crossed polarizers, and (iii) drawn azoBPA-6FDI-100 aligned  $45^\circ$  to the crossed polarizers, showing green birefringence color. c) Photogenerated stress with sequenced light irradiation of undrawn and drawn azoBPA-6FDI-100. The materials were preexposed to linearly polarized ( $E||x$ ) 445 nm light until reaching the equilibration and subsequently subjected to the sequenced light at a frequency of 0.25 Hz.

the azoBPA-6FDI-100 (subsequent to reaching a photostationary state) were monitored with sequenced light input. As previously reported, drawing aligns the azobenzene chromophores and correspondingly enhances the magnitude of the equilibrium deflection.<sup>[24]</sup> However, as shown in Figure 3a, the displacement of cantilevers prepared from undrawn and drawn azoBPA-6FDI (both at a photostationary state after 1 h of preexposure) shows undetectable variation in deflection when irradiated with sequenced irradiation at 1.2 Hz. As in our prior report,<sup>[24]</sup> drawing azoBPA-6FDI increases

the magnitude of the photogenerated stress from 0.16 to 1.9 MPa (Figure 3b). At this photostationary equilibrium condition, exposure of the undrawn and drawn azoBPA-6FDI-100 material to sequenced irradiation at 0.25 Hz generates significant changes in stress. For the undrawn azoBPA-6FDI-100 sample, the variation in photogenerated stress is  $\approx 40$  and 120 kPa in the drawn azoBPA-6FDI-100 samples. Accordingly, the photopiezoelectric signals observed in the laminates in Figure 2d, are attributable to variations in stress rather than variations in deflection.

## 4. Conclusions

In summary, a series of azobenzene-functionalized 6FDA-based polyimide copolymers were examined over a range of azobenzene concentrations. The photomechanical response, visualized in cantilever deflection experiments, increases in azobenzene concentration. Notably, the relaxation properties of the materials also vary—in which samples prepared with largest azobenzene concentration (and lowest modulus) do not show signs of stress retention. Uniaxial hot-drawing is employed to align azobenzene moieties in the materials to generate photopiezoelectric effects in laminates with PVDF. The chemical and physical modification techniques demonstrated a wide range of tailoring capability in photomechanical responses that can be transferred into electrical output.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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