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Ultra-High Actuation Stress Polymer Actuators as Light-Driven Artificial Muscles

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ABSTRACT: Remotely addressable actuators are of great interest in fields like microrobotics and smart textiles because of their simplicity, integrity, flexibility, and lightweight. However, most of the existing actuator systems are composed of complex assemblies and/or offer a low response rate. Here, the actuation performance of a light-driven, highly oriented film based on ultra-high molecular weight polyethylene (UHMW-PE), containing a photo-responsive additive, 2-(2*H*-benzotriazol-2-yl)-4,6-ditertpentylphenol (BZT), is reported. The material exhibits a fast (<1 s) and reversible photo-induced thermal response upon exposure to UV light, which results in an exceptionally high actuation stress (~70 MPa) at a low strain (<0.1%). The proposed actuation mechanism originates from light absorption by BZT and energy transfer into heat, in combination with the intrinsic high stiffness (~80 GPa) and a negative thermal expansion (NTE) of the oriented polymer films. This unique set of properties of this actuator, in particular the very high specific actuation stress, compared to existing organic and inorganic actuators, and the remote optical actuation, promises impact in fields related to soft robotics, composites, medical devices, optics, prosthetics, and smart textiles.

KEYWORDS: photo-response, oriented polymers, actuators, artificial muscles, specific actuation stress, negative thermal expansion

INTRODUCTION

Actuating materials and especially fibrous actuation materials like artificial muscles have been an active area of research for a number of decades.^{1–6} Extensive research and innovation has occurred in this field, and a wide range of inorganic (metallic and ceramics) and organic (polymeric) actuators have been reported. The selection of an appropriate actuator is highly application-driven requiring simplicity, feasibility, and flexibility and is often mainly based on properties such as actuation stress, response rate, reversibility, and actuation work.

Over the years, actuators have been developed and demonstrated based on shape-memory alloys and shape-memory polymers (SMPs),^{7–10} liquid crystal elastomers (LCE),^{11,12} electrostatics,¹³ piezoelectrics,^{14,15} conductive polymers,^{14,16} electrostrictive polymers,^{15,17} magnetostrictive materials,¹⁸ carbon nanotube fibers¹⁹ and yarns,²⁰ contractile polymer gels,²¹ coiled synthetic fibers,²² and hydrogels.²³ Each actuator has a specific range of stresses and response times, which make them suitable for applications such as robotics, medical devices, artificial organs, prosthetics, and other devices. However, most of the existing systems exhibit a low response rate and/or are composed of complex assemblies, hampering their use in confined spaces and specific applications like soft- and micro-robotics and functional textiles.

Baughman and co-workers²⁰ highlighted the need for an actuation system that triggers itself by agents in the

environment. Photo-actuation, using light as stimulus, is of practical importance as it does not require physical contact with the system to initiate the actuation and can be modulated precisely with respect to the wavelength of light, light intensity, and polarization direction. Moreover, it has the potential for rapid response, although this depends on the material's intrinsic properties. Photo-initiated polymer actuators have been produced based on liquid crystals, but these materials usually generate a low actuation stress (<5 MPa) at relatively high strain (>10%).^{24,25} Photochromic azobenzenes with long aliphatic tails have recently been introduced by our group in highly oriented ultra-high molecular weight polyethylene (UHMW-PE), which resulted in a high photo-actuation stress as a result of contraction of the high-modulus UHMW-PE film and which was believed to be the result of light-induced conformational changes in the azo compound.²⁶ However, the governing mechanism behind this photo-mechanical response remained a matter of scientific debate as photo-actuation might have been also partly the result of a thermally induced entropic

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Figure 1. (a) Proposed principal mechanism of photoactuation behavior of drawn UHMW-PE/BZT films upon UV exposure at a wavelength of 365 nm. (b) Stress-relaxation behavior of drawn UHMW-PE films ($\lambda = 60$) incorporating 0, 1, 2, and 5 wt % BZT upon cyclic UV exposure, showing the recorded actuation stress (MPa) generated as a function of time. The light blue area shows the UV exposure duration.

negative thermal expansion (NTE) effect rather than conformational changes of the azobenzenes.

High macromolecular orientation in semi-crystalline polymers like PE not only leads to a relatively high NTE²⁷ effect but also is a very efficient way to achieve a high modulus and strength in these polymers. Chain orientation and chain extension in polymer systems are necessary to exploit their intrinsic ultimate mechanical properties.²⁸ For instance, solution-cast UHMW-PE can be drawn to very high draw ratios (DRs) in the solid state and shows mechanical properties and thermal conductivity in the orientation direction similar to metals.^{29,30} Recently, our group has also shown that drawn PE films can also be made transparent by carefully tuning the drawing conditions or using additives or combination thereof.^{29,31} This optical transparency opens up the possibility to make photo-actuated films or tapes with a high specific Young's modulus and tensile strength.³²

Here, the photo-actuation of ultra-drawn UHMW-PE films containing a simple 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (BZT) photo-absorber is investigated in detail. A

photo-actuation mechanism based solely on the use of commercially available BZT and a light-induced entropic NTE effect would have significant technological advantages over a mechanism based on conformational changes in specially synthesized azobenzenes as reported in our previous work.²⁶ It is shown that a rather facile and unique class of fast photo-actuators based purely on thermally induced entropic actuation can be produced with an unprecedented high actuation stress (~ 70 MPa) at a low strain ($<0.1\%$) and with potential as high-performance artificial muscle fibers and photo-actuators.

RESULTS

In this study, a commercially available ultraviolet (UV) absorber (BZT) was used to generate heat on light absorption (at 365 nm) in ultra-drawn UHMW-PE. The extinction coefficient (ϵ) of the UV absorber was determined in xylene and in ultradrawn UHMW-PE (see the [Materials and Methods](#)) Section and was found to be $\sim 431\,000\text{ m}^2/\text{mol}$ in both cases. Based on this, the light intensity profile in films was

Figure 2. Influence of BZT content and draw ratio on the actuation stress of drawn UHMW-PE/BZT films upon UV exposure. (a) Actuation stress (MPa) as a function of UV exposure intensity (based on the LED current value) at various BZT concentrations (wt %) in drawn ($\lambda = 60$) PE films. (b–d) Actuation stress (MPa) as a function of UV exposure intensity (based on the LED current value) at variable draw ratios (40, 60, and 80) of UHMW-PE/BZT films.

calculated as a function of film thickness (Figure S1). As expected, it was found that an increased quantity of photo-absorber and an increased thickness of the polymeric film enhance the absorption of UV light, reduce the transmission, and create a steeper light gradient in the cross section of the films.

Gel-cast, solid-state drawn, UHMW-PE films with a draw ratio of 60, Young's modulus of ~ 80 GPa, and a BZT content between 0 and 5 wt % were produced (Figure S2a) as described in the Materials and Methods section. Ultraviolet–visible (UV–vis) measurements using linearly polarized light (Figure S3) indicate that the films are hardly dichroic in the absorption band of BZT, which indicates that polarization effects can hardly be expected. At a fixed draw ratio, Young's modulus of these films is not affected by the addition of BZT (Figure S4a). Yet, as expected, Young's modulus increases with increasing draw ratio (Figure S4b). Moreover, the stress-relaxation data (Figures S5 and S6) indicate that drawn films are linear viscoelastic at small pre-strains (between 0.2 and 0.8%), highly responsive, and reversible over a long-term periodic exposure.

MECHANICAL RESPONSE

The actuation performance of the oriented UHMW-PE/BZT films was evaluated by cyclic exposure of the constrained films to UV light at 365 nm in a tensile tester (Figures S2b and S6). The proposed principal mechanism of photo-actuation in these oriented polymeric films upon UV exposure is presented in Figure 1a. The stress-relaxation behavior of these highly oriented films was characterized within the viscoelastic regime ($\sim 0.8\%$ pre-strain). The typical light-driven actuation behavior of the films, at various BZT concentrations, is presented in Figure 1b.

Upon exposure to UV light, photons are absorbed by BZT and converted into heat. Due to the NTE coefficient of the

highly oriented, ultra-drawn polymer, a uniaxial contraction in the drawing direction is expected upon a temperature increase. The negative thermal expansion coefficient results in an actuation stress because the film is constrained between the two clamps ($\epsilon_0 \sim 0.8\%$) and not allowed to contract. Importantly, when the light is switched off, the stress reverts and returns to zero. This phenomenon is reversible, unlike most shape-memory polymers (SMPs), which are typically irreversible.³³ It is evident that even at low BZT concentrations of 1 wt %, the drawn PE films exhibit a rapid mechanical response to UV light with a significant actuation stress (Figure 1b). By optimizing the BZT content, a very high actuation stress can be achieved, with values in excess of 70 MPa (Figure 1b).

In Figure 2a, it is shown that the actuation stress increases approximately linearly with increasing light-emitting diode (LED) current (i.e., light intensity) when BZT is present, with peak stresses at different light intensity levels due to the amount of energy converted from various BZT loadings. At very high current levels, a maximum actuation stress can be observed followed by a descending trend, which is believed to be due to localized overheating and subsequent partial melting near the BZT compound. The morphology of the film was examined by scanning electron microscopy (SEM) both before and after exposure to UV light (Figure S7). The SEM images illustrate that no morphological changes are observed in the linear part of the actuation stress versus LED current graph (Figures 2a and S7). At very high light intensities, morphological changes are observed, which indicate partial relaxation of orientation or even complete melting (Figure S8).

The effect of light intensity (in terms of UV-LED current) on actuation stress at different BZT concentrations was also explored. A trend of increasing actuation stress with light intensity was observed (Figure 2a). It was also evident that, in the absence of photoabsorbing material, there was no actuation

Figure 3. (a) Photo-induced peak actuation stress of UHMW-PE/BZT films as a function of draw ratios for different BZT concentrations. (b) NTE coefficients of UHMW-PE films with a BZT concentration of 0 wt % at increased draw ratios.

Figure 4. Dynamic mechanical thermal analysis of UHMW-PE/BZT films. (a) Comparative behavior of thermally induced stress generated and NTE coefficient of UHMW-PE/BZT films over a temperature ramp as a function of draw ratios. (b) Comparative behavior of crystallinity and modulus of UHMW-PE/BZT films as a function of draw ratios. (c) Thermally induced stress generated at a constant strain value (0.1%) over a temperature ramp compared for films of different draw ratios.

stress generated even at very high light intensities. As expected, the actuation stress was BZT-concentration-dependent (Figure 2b–d). Increased light intensity provides more photon energy to be converted into heat by the photo-responsive materials, subsequently generating relatively rapid and higher actuation stresses. In parallel, a higher content of a photo-absorbing additive produces more phonons, leading to a higher actuation stress.

However, a careful investigation is required to determine the optimal amount of light intensity for a particular type of film (directly dependent on the BZT content and indirectly on film thickness) to harness the maximum possible actuation stress without damaging or degrading the film. Excessive light intensity may cause the film to lose its stiffness as a result of chain relaxation, which may cause it to expand rather than contract or may even get it to melt (Figure S8).³²

It might be possible that at higher light intensities, the temperature of the film during the thermal heating phase exceeds the α -relaxation temperature. Above the α -relaxation temperature, mobility within the polyethylene crystals increases and taut-tie molecules that connect the crystalline and amorphous regions can relax to a less strained state.^{34,35}

Heating causes the modulus to drop,³⁶ thus releasing the stress, leading to a visible sharp drop in the stress-relaxation curve.

In Figure 3a, it is shown that the maximum actuation stress is dependent on the draw ratio but not in a monotonic manner; a maximum in actuation stress is observed at a draw ratio of 60. The experimental data in Figure 3 also suggest that the actuation stress is a combined effect of various factors, mainly the concentration of photo-absorbing material (wt % BZT) and the draw ratio. The latter effect originates from the NTE of the oriented polymer film. The peak actuation stress for a given draw ratio will always be higher for higher BZT concentrations. However, the effect is nonlinear for a given BZT concentration with respect to the draw ratios. For example, the peak actuation stress is lowest for $\lambda = 80$ and highest for $\lambda = 60$, for a given BZT concentration. The observed effect is analogous to the NTE coefficients measured for the UHMW-PE films at different draw ratios (Figure 3b) using a dynamic mechanical analyzer (DMA).

As evident, the effect of draw ratio on actuation stress is in correspondence with the induced NTE (Figure 4a). Higher draw ratios lead to a higher modulus as a result of enhanced chain orientation and increased crystallinity (Figure 4b). Yet, at very high draw ratios, where crystallinity reaches close to

Figure 5. (a) Photothermal response observed upon UV exposure (0.9 A) of a drawn 5 wt % BZT/UHMW-PE film, showing a rapid response as heat is generated with light, leading to the generation of an actuation stress (light blue area shows the UV exposure interval). (b) Infrared images of a 1 wt % BZT/UHMW-PE film during a UV exposure cycle (10 s interval) showing a rapid thermal response by the embedded BZT within the film in terms of heat signature.

100%, amorphous regions diminish and the resultant NTE decreases as well (Figure 4), getting closer the NTE of polymer crystal lattice.³⁷ Beyond a certain draw ratio, the actuation stress starts to decrease instead of increasing, which is also evident from the thermally induced actuation stress within the films (Figure 4c). A similar effect was observed in Figure 2b–d where lower actuation stresses were observed for a draw ratio of 80.

It can be concluded that all of the above parameters and combinations thereof affected the actuation stress. By optimizing the BZT concentration, draw ratio, and light intensity, a maximum actuation stress of ~ 70 MPa was obtained.

■ THERMAL RESPONSE

As introduced in the previous section, the drawn UHMW-PE films are believed to undergo reversible contraction and exhibit a mechanical response in terms of a high actuation stress as a result of a thermal effect that originates from the heat energy produced by the embedded BZT (Figure 5a). A rapid (<1 s) and strong photo-thermal mechanical response (~ 70 MPa) is observed following the generation of heat upon UV exposure.

To confirm this hypothesis, a systematic study was performed that involved acquiring thermal images of these films upon UV exposure. An infrared thermal imaging camera detected the thermal energy radiating from the UHMW-PE film surface as the film heats up following UV light exposure. The thermal imaging system recorded the corresponding average temperature of the heated film in real time (Figure 5a). Yet, the absolute temperature recorded does not coincide with the actual temperature of the film, which would be far higher.

Figure 5b represents real-time thermal images of the film's surface upon UV exposure. The thermal effect observed is very responsive, rapid, and reversible. Thermal energy released by the random motion of BZT particles on UV absorption generates phonons and transfers the heat energy to neighboring UHMW-PE chains. In the presence of BZT, photons are absorbed at a specific wavelength upon UV exposure (Figure S9a), which is characteristic to BZT being an intrinsic UV-absorbing material. This light energy (photons) is then converted into heat energy (phonons), leading to a temperature rise within the film as observed through the thermal images.

Thermal images of neat UHMW-PE films without BZT were exposed to UV light as shown in Figure S10. Clearly, there is

no visible indication of any thermal effect upon UV exposure, even at high light intensity, which confirms that the thermal energy generated in the film upon UV exposure is solely the result of BZT. In the absence of photo-absorbing material, the light just passes through the film without being converted into heat energy, thus showing no signs of heating in the thermal images (Figure S10).

■ DISCUSSION

Like most other semi-crystalline viscoelastic polymers, undrawn isotropic PE exhibits a positive thermal expansion (PTE) coefficient. Oriented PE, on the other hand, shows a negative thermal expansion (NTE) coefficient in the drawing direction of the film. This NTE behavior of oriented PE originates from the presence of highly aligned polymer chains, leading to a chain contraction along the orientation direction upon heating. This effect explains the NTE behavior along the chain direction of a polymer crystal.^{37–39} Using this assumption, Chen et al. calculated, for a lattice of parallel chains having only carbon in the backbone, an NTE value of $-13 \times 10^{-6}/\text{K}$.³⁷

For oriented polymers with a lower crystallinity, the NTE may be up to an order of magnitude higher due to entropy-driven contraction of taut-tie molecules that link crystalline lamellae together and permit the load transfer between crystalline regions.³⁹ For polymers of higher crystallinity, because of the constraining effect of the crystal bridges, the NTE can reach values close to the thermal expansion of crystalline regions.²⁷ Yet, the contraction between these crystal blocks, due to an additional entropic effect of taut-tie amorphous molecules, can be significantly higher. The calculated NTE coefficients of our drawn films (Figure 3b) are much higher than the values calculated by Chen et al. for the crystalline lattice of PE.³⁷ This indicates that the photo-mechanical behavior we observe in the oriented UHMW-PE films is not merely the result of chain contraction in the crystal lattice but also partly an entropic effect related to an oriented amorphous phase. Values obtained for uniaxial oriented ($\lambda = 60$) UHMW-PE/BZT films were found to be in the range from -34×10^{-6} to $-41 \times 10^{-6}/\text{K}$ (Figure 4a) at a crystallinity of around 96% (Figure 4b), which confirms the presence of a combined crystalline and amorphous contraction effect.

At higher draw ratios, the further reduction of the amorphous phase as a result of an increased orientation and crystallinity leads to a reduction of the overall NTE values

(Figure 3b). This explains why lower actuation stresses were observed at high draw ratios (Figure 3a). We may therefore assume that there exists an optimum balance between crystallinity (amorphous vs crystalline phases) and the resultant NTE effect. For any specific concentration of the photo-responsive additive, a maximum actuation stress can be achieved by selecting an optimal draw ratio, while carefully adjusting the exposure intensity.

In Figures 6 and S11, the photo-driven actuator proposed in this research is compared to other actuators that are

Figure 6. Overview of specific actuation stress (actuation stress divided by material density) as a function of actuation strain. The current proposed UHMW-PE/BZT actuator system is labeled as “This work”. Data for comparison purposes has been acquired from the literature^{1,2,4,12,17,41} and subdivided into various classes (i.e., soft polymers, ceramics, composites, etc.) for clarity.

electrically, thermally, magnetically, chemically, and/or photo-driven. It is shown (Figure 6) that while being in the linear viscoelastic regime, our photo-actuated ultra-drawn UHMW-PE films generate the highest specific actuation stress, albeit at relatively low actuation strains (according to Hooke’s law $\epsilon = E/\sigma$). In this particular case, the specific actuation stress (actuation stress/density) is plotted which is important in applications in which weight needs to be minimized.⁴⁰

Although fundamentally dissimilar in terms of actuation stimulus and mechanism, the current actuator produces an almost 200 times higher actuation stress than natural muscle.¹ The current actuator clearly distinguishes itself from other soft polymer actuators, which are low in strength and stiffness and usually aim for high strains.⁴ It also outperforms ceramic and composite actuators with higher specific strength and modulus values,¹⁸ without compromising the flexibility, which is typical of the fibrous structure seen in artificial muscles. The oriented UHMW-PE actuator is also superior in specific actuation stress to other fiber-based artificial muscle actuators such as SMA fiber actuators^{41–43} and CNT fiber actuators.^{19,20} The photo-induced thermal response is very fast (<1 s) and reversible, even when BZT is only present in small amounts (~1 wt %), while the maximum specific actuation stress observed (>70 MPa) is the highest ever reported. Moreover, this photo-mechanical response was induced purely as a result of a thermally induced entropic NTE effect and not related to transformational changes as in the case of liquid crystal elastomers (LCE) or azobenzene compounds.^{24,26,40,41,44}

Future improvements of the current oriented UHMW-PE/BZT actuator should assess the true potential of this

technology in practical devices. For some applications like robotics and technical textiles, larger actuation strains, i.e., enhanced contraction during actuation, would be preferred. However, novel textile designs based on coiled fibers or twisted yarn-like assemblies could potentially generate larger actuation strokes.^{20,45} The potential of the current actuator mechanisms warrants further theoretical and experimental investigations, while future expansion into other polymeric and photo-active materials may open new avenues. One such avenue could be the triggering by natural UV light, as this could lead to many unique and practical applications. A physically contactless and powerless source would eliminate the need for any operational setup, while a tunable and optimized mechanism could generate a controllable mechanical response, rapidly and reversibly. Such a system could effortlessly harness the UV light from the environment for actuation and, therefore, could potentially be implemented in breathable fabrics, thermo-regulated textiles, and many other smart textile applications.

CONCLUSIONS

The present work introduces a simple and versatile fibrous polymer actuator system with unprecedented high specific actuation stress. It was shown that embedding a commercially available photo-responsive material like BZT in an intrinsically flexible but high-modulus polymer film or fiber can bring additional functionalities, producing a fast and reversible thermal actuation response that otherwise would not occur in such systems. The photo-mechanical behavior shown was purely the result of a thermally induced entropic NTE effect and not because of transformational changes in the conformation of its isomers, as in the case of polymer actuators based on liquid crystal elastomers or azobenzene compounds. The photo-induced thermal response is very fast (<1 s) and reversible, even at low BZT loadings (~1 wt %). An exceptionally high specific actuation stress of >70 MPa, the highest ever reported among all of today’s organic and inorganic actuator materials, was achieved at a strain of ~0.1% by optimizing the photo-absorber concentration, film’s draw ratio, and exposed light intensity. The unique combination of flexibility, robustness, high actuation stress, and high modulus holds promise for application of such fibrous actuators in fields related to soft robotics, composites, medical devices, optics, prosthetics, and smart textiles.

MATERIALS AND METHODS

The ultra-high molecular weight polyethylene (UHMW-PE) was acquired from DSM Stamylan UH 034 (Royal DSM, the Netherlands) with a weight-average molecular weight of approximately 3.3×10^6 g/mol. This polymer grade has a melting temperature (T_m) of around 140 °C and average particle size (D50) of 150 μ m.

2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol (BZT) ($C_{22}H_{29}N_3O$, with a density of 1.170 g/cm³) was provided by BASF (Tinuvin 328, Germany). Xylene ($C_6H_4(CH_3)_2$, 98.5% mixture of isomers) of Sigma-Aldrich (U.K.) was purchased from Thermo Fisher Scientific Inc. (the Netherlands). Paraffin oil was also purchased from Thermo Fisher Scientific Inc. (the Netherlands). All of these materials were used as received without further purification.

The methodology for making oriented films has been summarized in Figure S2a. UHMW-PE (2 w/v %) was first dissolved in xylene, and BZT was then added in different concentrations (0, 1, 2, and 5 wt %). The solution was first degassed in an ultrasonic bath for 30 min and then heated at 130 °C using an oil (silicon) bath until complete dissolution occurred. The viscous solution was poured in an

aluminum tray and left for drying in a fume hood. These gels were dried at room temperature (RT) for about 48–72 h to evaporate the solvent. Thin translucent isotropic sheets of UHMW-PE containing embedded BZT were obtained.

The UHMW-PE/BZT sheets were subsequently cut in specific dimensions and were drawn in a two-stage drawing process to draw ratios (DR) of $\lambda = 40, 60$, and 80 at $110\text{ }^{\circ}\text{C}$ at a cross-head speed of 100 mm/min in air using a universal tensile tester (Instron 5900R84, U.K.) equipped with an environmental chamber. Films were held at $110\text{ }^{\circ}\text{C}$ for about 10–15 min prior to drawing to allow a uniform sample temperature. The draw ratio of the drawn UHMW-PE/BZT films was determined from the displacement of ink marks, which were marked on the surface of the strips at regular intervals of 2 mm before the drawing process.³¹

To record and characterize the photo-mechanical response induced in the films upon UV exposure, a stress-relaxation experiment was devised comprising a Thorlabs 365 nm UV-LED (Thorlabs Vytran Europe, U.K.) in combination with a collimation lens, a DC-2200 driver, and an Instron 5900 universal tensile tester (U.K.) (Figure S2b).

Solid-state drawn UHMW-PE/BZT films, of 3.0 cm length each, were clamped (1 cm distance between clamps) in an Instron 5900R84 universal tensile tester at a distance of 13 cm from the UV-LED using a 0–1.7 A current and 5.0 V forward voltage supply, which was kept invariant for all samples tested. A pre-strain of 0.1% was set at the tensile tester for each sample. Samples were kept constrained in the clamps, usually for 1000 s, and were exposed to UV light after 100 s. Films were illuminated with 10 s intervals. Force values were recorded at 1 s intervals.

UV-vis absorption spectra of films in linearly polarized light were recorded at 700–250 nm by a spectrometer (PerkinElmer LAMBDA 750) using a polarizer at a scanning rate of 400 nm/min. Horizontally polarized incident light and vertically polarized incident light were introduced into the specimen, and the absorption intensities solely due to BZT molecules were recorded (Figure S3).

UV-vis experiments were performed on BZT, dissolved in xylene (in various concentrations i.e. $<0.01\text{ wt } \%$), using glass cuvettes and also on 3 cm long UHMW-PE/BZT film samples, which were characterized over a range of 300–700 nm with 1 nm intervals on a PerkinElmer LAMBDA 950 spectrophotometer at a 5 cm distance from the detector. The UHMW-PE/BZT film samples were sandwiched between two glass slides (transparent at wavelengths as low as 300 nm with no absorption in UVA spectrum) of about 1 mm thickness each. To avoid surface scattering during the test, the drawn UHMW-PE films were coated with paraffin oil. A baseline correction was performed. Data were recorded for light intensity profile (Figure S1) and for absorbance and transmittance values (Figure S9).

Young's modulus (E) of the drawn films was recorded using a universal tensile tester (Instron 5900R84, U.K.) at RT and at a cross-head speed of 100 mm/min.

Differential scanning calorimetry was carried out under a nitrogen flow using a differential scanning calorimetry (DSC) instrument (PerkinElmer DSC 4000). A heating and cooling cycle in a temperature range from RT to $200\text{ }^{\circ}\text{C}$ was applied. The UHMW-PE film samples (with and without BZT) were heated and cooled at a constant rate of $10\text{ }^{\circ}\text{C/min}$. The melting peak was determined, and the crystallinity was calculated through enthalpy measurements of the peak area.

A dynamic mechanical analyzer (TA Instruments Q800) with film clamps was used to carry out the thermal analysis. A constant heating rate ($5\text{ }^{\circ}\text{C/min}$) was applied throughout. Thermally induced stress and NTE of UHMW-PE films were measured over a temperature ramp under iso-strain and controlled force modes, respectively.

Scanning electron microscopy (SEM) (FEI Phenom, the Netherlands) analysis was carried out after sputtering the samples with gold to observe structure development after solid-state drawing as well as dispersion of BZT compound in the film and at a later stage to explore the UV-exposed surface of the films (Figure S7).

Optical microscopy (OM) was performed with an Olympus BX60 microscope (Japan) to investigate polymer alignment with respect to

the drawing direction and to analyze the surface morphology of unexposed and exposed (at varying intensities) film surfaces (Figure S8), using an optical analyzer.

The photo-mechanical behavior of the samples was investigated by irradiating the films with a high-intensity UV-LED (Thorlabs M365LPI, U.K.) with an adjustable collimation assembly having a wavelength of 365 nm.

Infrared images were taken with an infrared (IR) fusion technology camera (FLIR system, U.K.) to capture thermal images of the illuminated films. Thermographic data acquisition was carried out through the FLIR ResearchIR application associated with the IR camera.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c07684>.

Light intensity profile (S1); experimental procedure (S2); absorption behavior in polarized light (S3); modulus (S4); viscoelastic behavior (S5); photoinduced actuation behavior (S6); scanning electron microscopy (S7); optical microscopy (S8); absorption and transmission spectra (S9); thermographic analysis (S10); and absolute actuation stress (S11) (PDF)

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Notes

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