Fast, light-responsive, metal-like polymer actuators generating high stresses at low strain

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A lightweight actuator is fabricated by incorporating photo-responsive azobenzene dyes with polyethylene side chains. The long C78 side chains of the dyes facilitate dispersion within apolar ultra-drawn ultra-high molecular weight polyethylene films. The lightweight dichroic polymer films allow for a fast (<1 s) mechanical response to light, generating exceptionally high stress values at low strain typically found in hard robotics. These soft actuators can also attain oscillating stress wave responses using linearly polarized light.

**HIGHLIGHTS**

- Polyethylene functionalized photo-responsive azobenzene dyes
- Lightweight polymeric actuators with metal-like stress responses
- Oscillating stress wave responses generated in soft actuators
Fast, Light-Responsive, Metal-Like Polymer Actuators Generating High Stresses at Low Strain

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SUMMARY
Producing lightweight polymeric actuators able to generate high stresses typical of hard metals and/or ceramics remains challenging. The photo-mechanical responses of ultra-drawn ultra-high molecular weight polyethylene (UHMWPE) actuators containing azobenzene photo-switches with symmetrically attached polyethylene (PE) side chains are reported. Long PE side chains promote dispersion within the apolar UHMWPE matrix, and the ultra-drawn films are highly aligned. The ultra-drawn azobenzene-doped UHMWPE films have high Young’s moduli (~100 GPa) and are viscoelastic at room temperature at strains below 1%. The photo-mechanical response of the films is fast (<1 s), showing a high specific actuation stress response (>6 x 10^4 Pa (kg m^-3) s^-1) to UV or visible light at a low strain (~0.06%). The actuator responds to rotating linearly polarized light, causing a photo-induced stress wave response. Such rapid, high-stress, low-strain, photo-mechanical responses are unique in soft polymer systems with physical values approaching hard metals/ceramics.

INTRODUCTION
Actuators can generate mechanical stress, strain, and work in response to chemical, thermal, electrical, hydraulic, magnetic, pneumatic, and/or light stimuli. Both organic and inorganic materials have been extensively explored for developing actuators for applications in soft and hard robotics, respectively. Rigid-bodied inorganic ceramics and/or metals are generally stiff materials (E >> 1 GPa) that generate high stresses at low strains (ε < 1%) in less than 1 s upon applying an electrical stimulus. In contrast, softer materials (E < 1 GPa) are primarily made of viscoelastic macromolecules with exactly the opposite properties: that is, low stresses at high strains (ε >> 1%). As an example, metal-based actuators typically have an actuation stress of 20–500 MPa at a strain of 0.009%–0.3% while soft actuators, such as human muscle, hydrogels, and liquid crystalline systems, exhibit typical stress values of 0.06–4 MPa at 2%–90% strain. Finding lightweight alternatives for tasks commonly performed by hard robotics, which are normally constructed from heavy inorganic parts and actuated via electric stimuli, is challenging. Using light as stimulus is attractive for allowing untherted, controlled actuation. Here, we opt for fabricating lightweight, robust macromolecular actuators based on ultra-drawn ultra-high molecular weight polyethylene (UHMWPE), which are capable of generating high stresses at low strains using local light exposure, bridging the gap between electrically driven hard and light-driven soft actuators.

Progress and Potential
Lightweight polymeric actuators are traditionally not considered in applications such as robotics that demand high stress generation. A typical distinction is made between soft and hard actuators differing in modulus, actuation stress, and actuation strain: for example, hard actuators generate high stresses (20–500 MPa) at low strain, although being relatively heavy. Here, we report ultra-drawn ultra-high molecular weight polyethylene (UHMWPE) films doped with azobenzene dyes offering excellent mechanical properties and photo-mechanical stability combined with fast, remote response to (linearly polarized) light. These lightweight actuators bridge the gap between electrically driven hard and light-driven soft actuators generating stresses exceeding 60 MPa at low strain (~0.06%). Emerging device architectures, such as domestic robotics, stimuli-responsive valves, or pressure controllers, can significantly benefit from these polymer-based actuators strong enough to perform important tasks.
UHMWPE, a viscoelastic soft material, has outstanding metal-like mechanical properties after solid-state drawing at elevated temperature to ultra-high draw ratios. The resulting fibers and films contain highly oriented macromolecules, largely present in the form of chain-extended crystals, and attain maximum Young’s moduli of 100–180 GPa and tensile strengths of 3–5 GPa. Per unit weight, these lightweight materials outperform ceramics and metals, and therefore are used in demanding applications including life protection. Tethered, temperature-responsive UHMWPE-based actuators have been reported; however, by making these polymers light responsive their practical usage can be extended, enabling fast, untethered actuation.

To allow the UHMWPE to wirelessly respond to light, we synthesized photo-responsive azobenzene dyes with polyethylene (PE) side chains and incorporated them in the ultra-drawn films. The long aliphatic side chains of the dyes facilitate dispersion within the UHMWPE matrix, and the dyes become highly dichroic after solid-state drawing. This incorporation results in a fast (<1 s) mechanical response to light, generating exceptionally high specific actuation stresses (>6 × 10^4 Pa (kg m^-3)) at a strain of 0.06% in the stretched films. The mechanical response to light originates from the negative thermal expansion coefficient of the ultra-drawn UHMWPE in combination with the photo-thermal properties of the azo polymer. As a result, we generate mechanical values typical of hard robotics utilizing an ostensibly soft robotic material.

RESULTS AND DISCUSSION

Two azobenzene dyes with long PE chains were synthesized: C78-OH-AZO and C78-AZO (Figure 1A). The side chains are expected to reside in interfacial regions, possibly partially integrated into the crystal lattice, and/or in the amorphous regions of the apolar PE matrix. It is anticipated that the C78-OH-AZO dye has a short cis isomer lifetime, acting primarily as a photo-thermal dye, while in case of C78-AZO films the photo-mechanical effect will also contribute, as the lifetime of the cis isomer is relatively long. The PE chains were attached via K2CO3 base activated alkylation of 4,4'-dihydroxyazobenzene or (E)-4-((4-hydroxyphenyl)diazenyl)benzene-1,3-diol using iodopolyethylene alkylation reactant (PE-I) (Mw ~ 1220 g/mol, on average C78-I, 90% purity) with 4,4'-dihydroxyazobenzene or (E)-4-((4-hydroxyphenyl)diazenyl)benzene-1,3-diol. The Synthesis section details analytical data for the applied PE-I material, and reports on the synthesis and analytical characterization of both C78-AZO and C78-OH-AZO; high-temperature 1H nuclear magnetic resonance (NMR) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra are included, as well as high-temperature gel-permeation chromatography (HT-GPC) chromatograms (Figures S1–S4). Interpretation of the 1H NMR data indicate estimated purities of C78-AZO and C78-OH-AZO of about 73% and 61% (see Synthesis), respectively. The HT-GPC chromatograms prove conversion of iodopolyethylene PE-I into species with about a doubled molecular weight, in line with expectations. The MALDI-TOF mass spectra show arrays of peaks with masses attributable to C78-AZO (Figure 1B) as well as for C78-OH-AZO.

Ultra-drawn composite films were prepared as follows. UHMWPE, antioxidant, and azobenzene dyes were suspended and dissolved (2% [w/v]) in xylene at 130°C, cast in an aluminum tray, and dried under a fume hood for several days. The solution-cast, unstretched films were colored vibrant yellow (C78-AZO) or orange (C78-OH-AZO) depending on the presence or absence of the electron-donating hydroxy substituent. Solid-state drawing (at 120°C) of these films was performed to a
draw ratio (DR) of 60, resulting in highly dichroic films: the oriented molecules predominantly absorb light along the stretching direction (Figures 2A and 2B).19,20 The azobenzene molecules exhibit typical azobenzene absorption characteristics, indicating excellent miscibility (Figure S5). The azobenzene dye alignments were determined by measuring the order parameter (S), calculated using

\[ S = \frac{A_{\text{par}} - A_{\text{perp}}}{A_{\text{par}} + 2 \cdot A_{\text{perp}}} \]  

(Equation 1)

where \( A_{\text{par}} \) and \( A_{\text{perp}} \) are the absorbance for light polarized parallel and perpendicular to the drawing direction, respectively: totally random orientations result in \( S = 0 \) while perfect alignment is described by \( S = 1 \).21 After baseline correction for reflection, \( S \) values were found to be \( \geq 0.7 \) for both C78-AZO-doped and C78-OH-AZO doped films (Table S1). However, determining the order parameter is strongly influenced by the baseline correction.22 As a control, a hydroxyazobenzene derivative with short aliphatic side chains (C12-OH-AZO) was also incorporated into UHMWPE. UV-visible spectroscopy and X-ray diffraction evinced poor miscibility of the C12

Figure 1. Molecular Structures, MALDI-TOF-MS Spectra, and a Schematic of Azobenzene Dyes with Polyethylene Tails
(A) The two azobenzene molecules with PE side chains used in this study.
(B) MALDI-TOF-MS spectra recorded from the C78-AZO photo-switch.
(C) Simplified schematic illustration displaying postulated azobenzene incorporation and stress generation in ultra-drawn, doped UHMWPE composites during light exposure.
derivative within the PE matrix. Even at low doping content (≤0.10 mol %), absorption spectra show a blue shift of the absorption maximum, revealing probable H-type aggregation of this azo dye (Figures S6A and S6B). At higher doping content (0.22 mol %) the dye was found to form relatively large crystals during the casting procedure (Figure S6C).

Mechanical Characteristics and Photo-Mechanical Responses

Dispersing the azobenzene derivatives—up to 0.22 mol %—did not affect the storage modulus $E^*$ of the ultra-drawn UHMWPE host polymer (Figure S7A). At DR = 60, the crystallinity, orientation, and degree of chain extension increased significantly, leading to dynamic tensile moduli around 100 GPa. Films with a lower draw ratio (20 and 40, respectively) were also prepared, resulting in thicker, less crystalline films that absorbed more light with lower tensile moduli than the ultra-drawn films.

The mechanical responses of the azobenzene-doped UHMWPE films to UV and visible light illumination were examined during stress-relaxation experiments at strain levels ranging from $\varepsilon \sim 0.25\%$ to 1%, and revealed the composite films as being linear viscoelastic at room temperature up to at least 1% of strain (Figure S7B). The setup illustrated in Figure S8 was used to measure stress generation within the composite films at a constant strain of 1%. At $t = 0$ s, the films are strained, and the stress ($\sigma$) initially spikes and is measured as a function of time: stress relaxation by the polymer chains results in a decay of the stress, eventually reaching an apparent steady state. Repeated periodic light exposures (10 s on/off light switching between 100 and 400 s) at constant intensity demonstrated a consistently fast superimposed stress response (<1 s) on top of the relaxation-governed stress decay in the azobenzene-doped films, which disappeared at a similar timescale after switching off the light source (Figures 3A and 3B). It is most surprising that the photo-induced ($\sigma_{\text{photo}}$) response of these ultra-drawn composite films having ~100 GPa tensile moduli occurs in less than 1 s for both C78 dye-doped films. Remarkably, fast stress generation and relaxation also occurred regardless of whether the 365- or 405-nm light-emitting diode (LED) was used. Subsequent 10-s exposures using increasing intensities between 400 and 670 s increased the stress response (Figures 3C and 3D). By increasing the LED intensity the film is exposed to increasing temperatures, thereby lowering the relaxation modulus $G'(t)$, resulting in a faster relaxation response, which is evidenced by the progressive decay in

![Figure 2. Linear Dichroism of Azobenzene-Doped Ultra-Drawn Ultra-High Molecular Weight Polyethylene Films at Draw Ratio of 60](image-url) -- (A) 0.11 mol % C78-AZO. (B) 0.11 mol % C78-OH-AZO. Insets are photographs taken of the corresponding ultra-drawn films with the transmission axis of the polarizer at 0° indicated in white.
average stress. The observed stress decay, however, did not interfere with reproducibility of the values, consistent with the observed linear viscoelastic response and the knowledge that the heat dissipation is extremely efficient in the highly aligned polymer chains, calculated Fourier and Biot numbers indicated uniform and rapid conductive heat transfer over the thickness, impeding accurate film-temperature measurements. Additionally, light absorption by the azo dyes induced heat, which generated a contraction of the highly oriented PE chains.

Increasing the concentration of C78 azo dyes from 0.06 to 0.22 mol % within UHMWPE increased the photo-induced stress. Figures 4A and 4B display the responses to UV and visible light illumination as a function of the azobenzene concentration, revealing that increased C78 azobenzene content in the UHMWPE matrix indeed results in higher photo-induced stress (s\textsubscript{photo}). Illumination with a 365-nm LED source showed identical stress responses: ~46 and ~48 MPa for 0.22 mol % of C78-AZO and C78-OH-AZO, respectively. In contrast, excitation with a 405-nm LED resulted in diverging values for the different azobenzene derivatives. Remarkably, by incorporating 0.22 mol % of C78-OH-AZO exceptionally high mechanical stresses could be generated, even exceeding 60 MPa, the response being similar to a metallic linear actuator. At equal doping levels, the hydroxy-substituted azobenzene outperforms the C78-AZO. The absolute magnitude of the stresses depends on total light absorption of the azobenzene dye. Hydroxy substitution of the azobenzene dye (C78-OH-AZO) shifts the absorption spectra of the polymer films to the red (Figure 2), resulting in more overlap with the 405-nm LED emission spectrum.
The performances of the ultra-drawn films were compared by calculating the absorbed energy per square centimeter from the absorption and LED emission spectra. In Figures 4C and 4D the stress generated is shown as a function of the absorbed energy per excitation source at an equal dye concentration. Both C78 photo-switches perform similarly when illuminated with UV light, consistent with the nearly identical absorption of 365-nm light. Utilizing a more powerful 405-nm LED source favors the C78-OH-AZO dye, which absorbs nearly 200 mW cm$^{-2}$. Photo-induced stresses were found to scale with increasing dye concentration, regardless of the dye (Figures S9A–S9D). Remarkably, the nature of the dye did not influence the efficiency (photo-induced stress per absorbed mW cm$^{-2}$), as both generated large photo-induced stresses at identical absorbed energy levels.\textsuperscript{34} Solid-state stretching of UHMWPE films or fibers significantly alters the structure of the crystalline and amorphous domains. At higher draw ratios UHMWPE increases in crystallinity, which leads to a smaller amorphous fraction.\textsuperscript{25,26,35} In other words, drawing the films significantly imposes conformational constraints on the azobenzene photo-switches, the cores of which are expected to reside in the non-crystalline amorphous regions, restricting trans-cis photo-isomerization and favoring cis-trans back isomerization.\textsuperscript{17,36} The cis C78-AZO isomer could only be identified in modestly drawn—DR = 20—films containing 0.22 mol % of the C78-AZO (Figure S10) suggesting that the cis isomer lifetime is reduced in the ultra-drawn polymer films. Therefore, we hypothesize that photo-excitation of both azobenzene photo-switches are predominantly generating heat, which is transferred via the highly oriented aliphatic side chains embedded in the matrix. The well-dispersed azobenzene derivatives thus reside in non-crystalline amorphous regions, possibly anchoring the PE tails to the crystal faces.
or in the (aligned) amorphous regions, not distorting the UHMWPE lattice (Figure S11) but simply conducting heat to the extended-chain PE matrix and generating large mechanical stresses. The fact that no photo-induced stress is observed in water for either film supports the hypothesis that both C78 dopants act as photo-thermal agents (Figure S12). The photo-thermal response of the azobenzene depends on the miscibility with the UHMWPE matrix, yet despite poor miscibility the short C12 side chain azobenzene still attained a photo-induced stress of \( \frac{s}{C_24} \sim 30 \text{ MPa} \) (Figures S13A and S13B). In fact, even the commercially available photo-thermal 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (BZT) dyes could be embedded into ultra-drawn UHMWPE, enabling stress generation in response to UV light (Figure S13C). However, stress generation using this photo-thermal dye was found to be less efficient than for azobenzene-doped films (Figure S13D). This experiment reveals that stress generation using UV or visible light exposure does not necessarily require good dispersion within the PE and that good miscibility is crucial in realizing the exceptionally high stresses.

Performance among Soft and Hard Robotic Actuators

To our knowledge, macromolecular actuators that operate at low strain values capable of generating such high stresses \( (\sigma_{\text{photo}} > 60 \text{ MPa}) \) have never been reported previously. These novel, lightweight films show untethered, fast responses to local UV and/or visible light exposure while maintaining extremely high storage moduli. Additionally, periodic light exposure of azobenzene-doped films has shown excellent photo-mechanical stability over at least \( \sim 2,600 \) cycles without any observable loss in photo-induced stress (Figures S14 and S15). Moreover, the highly aligned dyes swiftly respond to rotating linearly polarized light (Figure 5A), causing a photo-induced stress wave response. As the polarization state equals the drawing direction of the dichroic films, i.e., at \( 0^\circ \) and \( 180^\circ \) maxima in actuation stress are found (Figure S16), this fast, oscillating mechanical response enables the creation of periodic stresses under constant light intensities.

The specific actuation stress is calculated by dividing the photo-induced stress by the density of the material:

\[
\text{Specific actuation stress} = \frac{\sigma_{\text{actuation}}}{\rho}.
\]

(Equation 2)
For highly crystalline, ultra-drawn UHMWPE, a density of 975 kg/m$^3$ was used. At low strain (1%), the composite films photo-mechanically respond to UV or visible light by generating high specific actuation stresses of $>6 \times 10^4$ Pa (kg m$^{-3}$)$^{-1}$. The features of our macromolecular actuators and other soft and hard actuators are presented in Figure 5B, which displays the specific actuation stress (per unit weight) as a function of actuation strain. Note that the azobenzene-doped materials are the only materials that generate stress in response to UV and/or visible light in Figure 5B; the rest are all temperature driven. Despite remote triggering of the system, light-to-heat conversion plays a crucial role in inducing stress in the azobenzene-doped materials. Among all the actuators, hard (depicted in gray/black) or soft (shown in white and green), the UHMWPE composites act as a unique hybrid soft-hard actuator. These lightweight UHMWPE composites could bend an inorganic high-modulus materials using visible light exposure: the film ends of a 0.22 mol % C78-OH-AZO composite were fixed to an aluminum strip using UV-curable glue, and visible light exposure resulted in reversible hinge-like bending of the strip thanks to the mismatch in thermal expansion (Video S1 and Figure S17). In device architectures as proposed by the groups of Haines, Wu, and Sutton, blending in PE-functionalized azobenzene permits a fast untethered stress response to local or polarization-sensitive light exposure.

Conclusions
Unique PE (C78) azobenzene photo-switches were synthesized and embedded into UHMWPE tapes. The PE chains of the dyes facilitated dispersion within the highly apolar PE matrix, dispersing much better in comparison with azobenzenes with shorter (n = 12) PE tails or the small-molecule UV absorber BZT, and resulted in well-aligned photo-responsive composites upon solid-state stretching. The viscoelastic macromolecules were found to have tensile moduli of $\sim 100$ GPa, comparable with hard linear actuators. Regardless of the photo-absorber (C78, C12, or BZT) or excitation source (365- or 405-nm LEDs), large photo-induced stresses were generated in ultra-drawn (DR = 60) composite films. However, the increased miscibility of the C78 derivatives in the UHMWPE allowed the absorption of more incident excitation light, and during stress-relaxation experiments photo-induced stresses exceeding 60 MPa were obtained at a strain of $\sim 0.06\%$. The exceptionally high stresses generated by simple exposure to light in what normally would be considered a soft actuator material are similar to those found in light-insensitive hard actuators embodying a new class of fast-responding (<1 s) hybrid soft-hard linear actuators.

EXPERIMENTAL PROCEDURES
Materials
Ultra-high molecular weight grade PE ($M_n = 310$ kg/mol, $M_w = 2,170$ kg/mol) and iodopolyethylene PE-I (supplied from Activation; $M_w = 1,220$ g/mol, relating to on average C78-I) were kindly supplied by DSM. Azobenzene dopants C78-AZO and C78-OH-AZO were synthesized in-house starting from PE-I (see Synthesis for details of PE-I, C78-AZO, and C78-OH-AZO). Azobenzene dopant C12-OH-AZO was synthesized starting from 1-bromododecane. Irganox 1010, a phenolic antioxidant, was acquired from BASF. Xylene, orthodichlorobenzene (ODCB), methyl ethyl ketone (MEK), 1-bromododecane, and chloroform were purchased from Sigma-Aldrich. Silicon oil was acquired from Thermo Fisher Scientific. All reagents were used as received without further purification.

Synthesis
General Preparation
All reagents, chemicals, materials, and solvents were obtained from commercial sources and used as received. All solvents were of AR quality. $^1$H NMR spectra
were recorded on a Bruker Avance III HD spectrometer at 80°C. Chemical shifts are reported at room temperature in ppm downfield from TMS (tetramethylsilane). Abbreviations used for splitting patterns are: s, singlet; d, doublet; t, triplet; m, multiplet. MALDI-TOF-MS was measured on a Bruker Autoflex Speed using 2-((2E)-3-(4-t-butylphenyl)-2-methylprop-2-enylidene)malononitrile (DCTB) as matrix. For the MALDI-TOF-MS measurements, first a dried film of the matrix was prepared by drop casting a tetrahydrofuran solution (20 mg/mL) of DCTB. Next, the product, C78-AZO or C78-OH-AZO, was dissolved in hot ODCB (1 mg/mL), and one drop of the solution was pipetted on top of the DCTB film. The resulting two-layered spot was dried prior to MS analysis. HT-GPC was performed at 140°C using Agilent Technology PL-GPC-220 equipment, applying a Mixed-B (300 × 7.5 mm [internal diameter]) column (Agilent Technology; molecular weight up to about 4,000,000 as based on polystyrene standards). ODCB was used as the mobile phase at a flow rate of 1 mL/min. Sample solution concentration: 10 mg/mL. Refractive index detection gave molecular weight (distribution) data relative to polystyrene standards.

PE-I
The iodopolyethylene PE-I provided purity information about 90% by weight. 1H NMR (400 MHz, Toluene-d8, 80°C) δ 2.8 (CH2- I , t, 2 H), 1.6 (CH2, m, 2 H), 1.5–1.1 (CH2 groups), 0.9 (CH3, t, 3 H). The 1H NMR spectrum in toluene-d8 for PE-I is shown in Figure S1A. MALDI-TOF-MS analysis of the PE-I material proved unsuccessful. HT-GPC shows an Mn, of 1430 Da, an Mw (mass at peak of trace) of 1,447 Da, and a PD (polydispersity) of 1.36 (see Figure S1F for the GPC trace).

C78-AZO
In a reaction flask, 4,4'-dihydroxyazabenzene (0.43 g, 2.01 mmol), iodopolyethylene PE-I (5.6 g, 4.13 mmol C78-I, Mn = 1,220) and K2CO3 (2.21 g, 16 mmol) were dissolved in 77 mL of dimethylformamide (DMF) and the mixture was heated to 90°C (Figure 6). After 40 h of stirring at 90°C, a thick yellow suspension had formed. The reaction mixture was filtrated while still hot, and the residue was washed consecutively with hot DMF, hot water (3 ×), and acetone (3 ×). The light-yellow solid was dried in vacuo at 40°C to yield 5.30 g (110%) of material. The theoretical average molecular weight for the C78-AZO product is 2,400 Da.

1H NMR (400 MHz, Toluene-d8, 80°C) δ 8.00 (d, J = 8.5 Hz, 4H), 6.90 (d, J = 8.4 Hz, 4H), 3.77 (t, J = 6.5 Hz, 4H), 1.79–1.64 (m, 4H), 1.37 (multiple CH2 groups), 0.93 (t, J = 6.6 Hz, 6H). MALDI-TOF-MS (reflector mode, DCTB matrix): peaks observed from about m/z = 1,400 to about 2,800 with Δm/z = 28.02 g/mol. Simulated mass for the C60-AZO oligomer (C132H250N2O2): m/z = 1,895.95 g/mol, observed m/z = 1,896.19 g/mol for the [M-radical]+. Note that a subset of minor peaks has a periodicity of 58 Da. This array of peaks does not relate to the product, but to poly(propylene oxide) contaminant that is present in plastic consumables as used.

Figure 6. The Synthesis of Disubstituted Azobenzene Dyes C78-AZO and C78-OH-AZO
in the MALDI-TOF-MS sample preparation. HT-GPC shows an $M_n$ of 2,111 Da, an $M_p$ of 3,376 Da, and a PD of 1.61 (see Figure S1F for the GPC trace).

The disubstituted product contains contaminants: excess iodopolyethylene ($\delta = 2.8$ ppm for CH$_2$-I), dehydroiodinated PE ($\delta = 5.0$ ppm for the eliminated -CH=CH$_2$ end group), non-functionalized PE ($\delta = 0.93$ ppm for CH$_3$), and possibly a minor amount of monosubstituted product. The integral at $\delta = 3.77$ ppm for the two CH$_2$-O methylenes corresponds very well to the integrals for the Ar–H protons at $\delta = 8.00$ and 6.90 ppm, demonstrating that mostly full conversion to the disubstituted product has taken place. The contaminants cannot be removed by purification due to their high resemblance to the disubstituted product material and their low solubilities. Estimated purity of C78-AZO based on $^1$H NMR analysis: about 73% by weight (with the integral of 4.00 for the CH$_2$-O methylenes, the (CH$_2$)$_n$ integral is expected to be 300 for C78-AZO; however, an integral of 412 is recorded).

The $^1$H NMR spectrum and the MALDI-TOF-MS mass spectrum for C78-AZO are provided in Figures S1B and S1C, respectively.

C78-OH-AZO

In a reaction flask, (E)-4-((4-hydroxyphenyl)diazenyl)benzene-1,3-diol (0.46 g, 2.00 mmol), iodopolyethylene PE-I (5.6 g, 4.13 mmol C78-I, $M_w = 1,220$), and K$_2$CO$_3$ (2.21 g, 16 mmol) were dissolved in MEK (77 mL) and the mixture was heated to reflux. After 40 h at reflux, a thick red/orange suspension had formed. The reaction mixture was filtrated while still hot, and the residue was consecutively washed with hot MEK, hot water (4 x), and acetone (3 x). The red/orange solid was dried in vacuo at 40°C to yield 5.35 g (111%) of material. The theoretical average molecular weight for the C78-OH-AZO product is 2,416 Da.

$^1$H NMR (400 MHz, Toluene-$d_8$) $\delta$ 13.55 (s, 1H), 7.80 (d, $J = 8.4$, 1H), 7.69 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 6.60 (d, $J = 2.7$ Hz, 1H), 6.56 (s, 1H), 3.74 (t, $J = 6.0$ Hz, 4H), 1.71 (m, 4H), 1.37 (multiple CH$_2$ groups), 0.92 (t, $J = 4.7$ Hz, 6H). MALDI-TOF-MS (reflector mode, DCTB matrix): peaks observed peaks from about $m/z = 1,200$ to about 4,000 with $\Delta m/z = 28.02$ g/mol. Simulated mass for C50-OH-AZO (C$_{112}$H$_{210}$N$_2$O$_3$): $m/z = 1,631.63$ g/mol, observed $m/z = 1,632.83$ g/mol for the [M + H]$^+$ cation. HT-GPC shows an $M_n$ of 2,257 Da, an $M_p$ of 3,215 Da, and a PD of 1.49 (see Figure S1F for the GPC trace).

The disubstituted product contains contaminants: excess iodopolyethylene ($\delta = 2.8$ ppm for CH$_2$-I), dehydroiodinated PE ($\delta = 5.0$ ppm for the eliminated -CH=CH$_2$ end group), and non-functionalized PE ($\delta = 0.92$ ppm for CH$_3$). The integral at $\delta = 3.74$ ppm for the two CH$_2$-O methylenes corresponds well to the integrals for the OH and Ar–H protons at 13.55 and between $\delta = 7.80$ and 6.56 ppm, respectively, demonstrating that the desired disubstituted product is the main component. Signals around $\delta = 8.0$ and 4.0 ppm presumably indicate the presence of minor amounts of monosubstituted, wrongly disubstituted isomer, and/or trisubstituted product. The contaminants cannot be removed by purification due to their high resemblance to the desired disubstituted product material and to their low solubilities. Estimated purity of C78-OH-AZO based on $^1$H NMR analysis: about 61% by weight (with the integral of 4.00 for the CH$_2$-O methylenes, the (CH$_2$)$_n$ integral is expected to be 300 for C78-OH-AZO; however, an integral of 493 is recorded).

The $^1$H NMR spectrum and the MALDI-TOF-MS mass spectrum for C78-OH-AZO are provided in Figures S1D and S1E, respectively.
C12-OH-AZO

The reaction mixture of (E)-4-((4-hydroxyphenyl)diazenyl)benzene-1,3-diol (100 mg, 0.434 mmol), 1-bromododecane (216.6 mg, 0.868 mmol), K₂CO₃ (138.2 mg, 1.30 mmol), and acetone (5 mL) was refluxed for 24 h. After K₂CO₃ was filtered out of the reaction mixture, acetone was evaporated under reduced pressure. The crude product was purified with silica-column chromatography followed by the recrystallization from acetone to yield 201 mg of brown solid C12-OH-AZO (82%).

¹H NMR (400 MHz, CDCl₃) δ 13.68 (s, 1H), 7.79–7.71 (m, 3H), 6.98 (d, J = 9.1 Hz, 2H), 6.58 (dd, J = 8.9, 2.6 Hz, 1H), 6.45 (d, J = 2.6 Hz, 1H), 4.02 (q, J = 6.5 Hz, 4H), 1.85–1.75 (m, 4H), 1.54–1.41 (m, 4H), 1.40–1.21 (m, 32H), 0.88 (t, J = 6.9 Hz, 6H). MALDI-TOF-MS (reflector mode, DCTB matrix): m/z 567.0 (calc. [M + H]⁺ = 567.87).

Methods
Preparation of Stretched UHMWPE Composites

The composite films were prepared following a conventional solution-(gel)-casting procedure: the individual components were suspended in xylene, trapped air was removed by applying a vacuum, and heating (130°C) under continuous stirring was applied until the Weissenberg effect occurred. The molar percentage of dye was calculated with respect to 7.1 × 10⁻² mol of UHMWPE (m₀ = 28 g/mol) and 4.2 × 10⁻⁶ mol of Irganox 1010. After the Weissenberg effect, the solution was kept in an oil bath for 1 h before being cast in an 8 × 8-cm² aluminum tray at room temperature. Xylene was evaporated for >4 days under a fume hood (at room temperature), yielding films of uniform thickness. From the as-cast films, 25-mm long and 10-mm wide tapes were cut and stretched to a DR of 60 at 120°C, yielding thin films of 10–12 μm.

Characterization

The absorption spectra of the composite films were recorded on a PerkinElmer Lambda 750 spectrophotometer equipped with a 150-mm integrating sphere. The composite films were placed between 3 × 3-cm² quartz glass slides with a droplet of silicon oil (refractive index ~1.41) to reduce surface light scattering. A baseline correction was performed.

A JASCO V-650 spectrophotometer equipped with a JASCO CTU-100 heating unit was utilized to measure absorption spectra at 100°C in quartz glass cuvettes.

Dynamic mechanical analysis was performed on composite films using a DMA 850 TA apparatus. At a constant frequency and amplitude (1 Hz and 10 μm, respectively), 30-mm-long samples were examined to measure dynamic tensile moduli. Stress-relaxation experiments were conducted using 1% strain and a 0.3 N pre-load. To test the photo-induced response of the composites, we employed 365-nm and 405-nm LEDs (Thorlabs M365L2 and M455L3). Oscillating mechanical response was examined using rotating linear polarized light (10LP-UV, Newport; mounted in a rotating stage, Thorlabs). All experiments were performed at ambient conditions.

X-ray diffraction experiments were executed using a Ganesha SAXS system equipped with a GeniX-Cu ultralow divergence source producing X-ray photons (λ = 1.54 Å, flux of 1 × 10⁸ ph s⁻¹). Diffraction patterns were recorded on a Dectris Pilatus 300K silicon pixel detector. Wide-angle measurements were performed at a 91-mm sample-to-detector distance utilizing the diffraction peaks of a Silver Behenate standard for calibration of the q-range.
REFERENCES


