Supporting Information

Amplified photo-responses in sequentially polymerized azobenzene-containing polymer networks: the role of isomer interconnection

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1. Materials

All the commercial materials used in this study were purchased from Sigma Aldrich with the highest purity and used without further purification unless stated otherwise. The thermal initiator di-tert-butyl peroxide (DTBP, > 98%) was purchased from Tokyo Chemical Industry. 4-Hydroxyphenyl-4-hydroxy benzoate (>98%) was purchased from Alfa Chemistry. Glass cell coating agent "Ease ReleaseTM 200, Smooth-On, Inc." was degassed and diluted 5 times with n-hexane before the spin coating procedure. Tetrahydrofuran (THF), dimethylformamide (DMF), methanol (MeOH), dichloromethane (DCM), n-hexane (n-Hex) and ethyl acetate (EtOAc) were distilled and dried over activated molecular sieves (3 or 4 Å, Daejung Chemicals) for 48 h before use. Acryloyl chloride (Wako, 97%) and allyl bromide (Alfa Chemistry, 99%) were distilled in the dark and stored in amber vials 5 h before use.

2. Monomer synthesis methods

• Synthesis of 4-(4-hydroxy-phenylazo)benzoic acid.

The synthesis of this compound follows the previously reported di-azo coupling procedures. (yield: 15.9 g, 93.7%) ¹H NMR (500 MHz, deuterated tetrahydrofuran (THF- d_8)) δ 8.14 (d, J = 8.2 Hz, 2H), 7.90 – 7.83 (m, 4H), 6.93 – 6.87 (m, 2H).

• Synthesis of 4-((4-(allyloxy)phenyl)diazenyl)benzoic acid (1).

4-(4-hydroxy-phenylazo)benzoic acid (2.4 g, 10 mmol) and K_2CO_3 (5.52 g, 40 mmol) were dissolved in 30 ml of dimethylformamide (DMF). The mixture was thoroughly mixed for 1 h at 80 °C before allyl bromide (3.6 ml, 40 mmol) was added. The suspension was further reacted for 5 h at 80 °C and poured into 200 ml of deionized (DI) water. The mixture was extracted with EtOAc (50 ml *2) and the organic layer was washed thoroughly with aqueous NaHCO₃ solution and dried over anhydrous MgSO₄. After evaporation of the solvent, the intermediate was dissolved in MeOH/H₂O mixture with KOH (2.3 g, 40 mmol) and refluxed for 5 h. After the reaction, methanol was evaporated from the mixture and the remaining solution was acidified by 1N HCl until the pH was less than 3. The precipitate was collected and washed several times with DI water. The crude product was recrystallized in acetic acid to yield the target product. (yield: 2.03 g, 72%) ¹H NMR (500 MHz, chloroform-*d*) δ 8.22 (d, *J* = 8.6 Hz, 2H), 8.00 – 7.90 (m, 4H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.15 – 6.03 (m, 1H), 5.46 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.35 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.65 (dt, *J* = 5.3, 1.6 Hz, 2H).

• Synthesis of 3-hydroxypropyl 4-((4-(allyloxy)phenyl) diazenyl)benzoate (2).

Product **1** (1.4 g, 5 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.9 ml, 6 mmol) were thoroughly mixed in DMF (10 ml) for 1 h before 3-chloro-1-propanol (0.52 ml, 6 mmol) was added. The mixture was then reacted at 120 °C for 5 h. After the reaction, the mixture was poured into 100 ml of DI water and extracted with dichloromethane (DCM) (50 ml *2). The organic layer was washed thoroughly with aqueous NaHCO₃ solution and dried over anhydrous MgSO₄. After evaporating the solvent, the crude product was purified by recrystallization in methanol to give the target product. (yield: 1.15 g, 69%) ¹H NMR (500 MHz, chloroform-*d*) δ 8.17 (d, *J* = 8.6 Hz, 2H), 8.00 – 7.86 (m, 4H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.14 – 6.02 (m, 1H), 5.46 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.34 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.64 (dt, *J* = 5.3, 1.6 Hz, 2H), 4.53 (t, *J* = 6.1 Hz, 2H), 3.81 (q, *J* = 5.5 Hz, 2H), 2.04 (p, *J* = 6.1 Hz, 2H), 1.90 (s, 1H).

• Synthesis of 3-(acryloyloxy)propyl 4-((4-(allyloxy) phenyl)diazenyl)benzoate (**AB-azo**).

Product 2 (1.36 g, 4 mmol), triethylamine (TEA) (1.4 ml, 8 mmol) and a trace amount of mequinol (MEHQ) was added to dry THF (20 ml) and cooled to 0 °C. A mixture of acryloyl

chloride (0.65 ml, 8 mmol) in THF (10 ml) was added dropwise to the suspension. After stirring for 1 h under argon atmosphere, the reaction was left at room temperature for 12 h before 200 ml of aqueous NaHCO₃ was poured into the reaction vessel. The resultant suspension was extracted with DCM (50 ml * 2) and the organic layer was washed with DI water and dried over MgSO₄. After evaporation of the solvent, the crude product was purified by column chromatography (eluent: EtOAc: n-Hex = 1: 2, v/v) and recrystallized from MeOH to give the final orange crystal product. (yield: 0.98 g, 62%) ¹H NMR (500 MHz, chloroform-*d*) δ 8.17 (d, *J* = 8.6 Hz, 2H), 8.00 – 7.86 (m, 4H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.43 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.18 – 6.03 (m, 2H), 5.84 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.46 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.34 (dq, *J* = 10.6, 1.4 Hz, 1H), 4.64 (dt, *J* = 5.3, 1.5 Hz, 2H), 4.47 (t, *J* = 6.3 Hz, 2H), 4.37 (t, *J* = 6.2 Hz, 2H), 2.20 (p, *J* = 6.3 Hz, 2H).

• Synthesis of 3-hydroxypropyl 4-((4-(3-hydroxypropoxy)phenyl)diazenyl)benzoate (**3**).

4-(4-hydroxy-phenylazo) benzoic acid (4.8 g, 20 mmol), potassium iodide (KI, 9.96 g ,60 mmol), DBU (9 ml, 60 mmol) were mixed thoroughly in 40 ml of DMF. 3-Chloro-1-propanol (60 mmol, 5.12 ml) was added dropwise into the mixture and further mixed for 0.5 h at room temperature. The reaction took place at 80 °C for 5 h and was terminated by adding 500 ml of 0.1 M HCl solution. The resultant suspension was extracted with EtOAc (50 ml *3) and the organic layer was washed with DI water and dried over MgSO₄. Finally, the solvent was evaporated, and the residue was recrystallized twice from MeOH to give orange crystals (yield: 3.5 g, 50%). ¹H NMR (500 MHz, chloroform-*d*) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 9.1 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 9.1 Hz, 2H), 4.53 (t, *J* = 6.1 Hz, 2H), 4.23 (t, *J* = 6.0 Hz, 2H), 3.90 (s, 2H), 3.81 (s, 2H), 2.10 (p, *J* = 6.0 Hz, 2H), 2.04 (p, *J* = 6.1 Hz, 2H).

• Synthesis of 3-(acryloyloxy)propyl 4-((4-(3-(acryloyloxy) propoxy)phenyl)diazenyl)benzoate (**DA-azo**).

This procedure is similar to the **AB-azo** synthesis procedure. The only difference is the amount of acryloyl chloride (3 molar equivalents of product **3**). The yield is 2.4 g (62%) after purification. ¹H NMR (500 MHz, chloroform-*d*) δ 8.17 (d, *J* = 8.7 Hz, 2H), 8.01 – 7.85 (m, 4H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.43 (dt, *J* = 17.3, 1.2 Hz, 2H), 6.14 (ddd, *J* = 17.3, 10.4, 3.8 Hz, 2H), 5.85 (ddd, *J* = 10.4, 2.6, 1.5 Hz, 2H), 4.47 (t, *J* = 6.3 Hz, 2H), 4.38 (dt, *J* = 8.3, 6.3 Hz, 4H), 4.17 (t, *J* = 6.2 Hz, 2H), 2.21 (dp, *J* = 7.8, 6.2 Hz, 4H).

• Synthesis of 4-allyloxyphenyl-4-allyloxybenzoate (**APAB**).

In a two-neck round-bottom flask, 11.512 g (50 mmol) of 4-hydroxyphenyl-4-hydroxybenzoate, K₂CO₃ (130 mmol, 17.97 g) and a trace amount of potassium iodide (KI) were refluxed in 100 ml of acetone for 1 h. Allyl bromide (150 mmol, 12.7 ml) in 20 ml of acetone was then added into the suspension dropwise. After refluxing for another 48 h under vigorous stirring, the excessive solvent and allyl bromide were evaporated under vacuum. When the system cooled down to room temperature, DI water was poured into the flask and the precipitate was collected by filtration. The crude product was recrystallized in methanol twice to give the pure white target product (yield: 13.8 g, 89%). ¹H NMR (500 MHz, chloroform-*d*) δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.07 (ddtd, *J* = 17.3, 10.6, 5.3, 2.7 Hz, 2H), 5.44 (ddq, *J* = 17.3, 9.9, 1.6 Hz, 2H), 5.32 (ddq, *J* = 18.9, 10.5, 1.4 Hz, 2H), 4.63 (dt, *J* = 5.2, 1.5 Hz, 2H), 4.54 (dt, *J* = 5.3, 1.5 Hz, 2H).

3. Characterization Methodologies

• Real-time Fourier-transform infrared spectroscopy (FTIR) characterization.

Real-time FTIR analysis was conducted on a Nicolet[™] iS5 FTIR spectrometer equipped with the iD1 Transmission accessory. The monomer mixture in toluene (20 wt%) and the designated amount of amine catalyst were prepared separately. Right before the tests, the monomers and catalyst were mixed vigorously and sandwiched into a demountable liquid cell (KBr plates with 250 µm spacers). Each spectrum was averaged over 4 scans and collected every 20 s to monitor the reaction kinetics. The conversion of each functional group was calculated by monitoring the disappearance of its characteristic peak intensity.

• UV-Visible (UV-Vis) spectroscopy characterization.

The UV-Vis spectra of the tested samples were measured on a UV-Vis spectrometer (Mega-2100, Scinco) at room temperature (25 °C) at a scanning rate of 300 nm/min. Isomerization of the azobenzene monomer was measured in quartz cuvettes (1 cm pathlength) in the single-cell holder. A 1×10^{-4} M DA-azo solution in chloroform was used as the standard. Thin film transmittance was measured in the integrating sphere setup.

• Nuclear magnetic resonance (NMR) characterization.

The NMR spectra of the synthesized compounds were recorded on an AVANCE III 500 (Bruker) spectrometer. Samples (5 wt%) of the compounds were prepared in deuterated solvent right before data collection.

• Gel permeation chromatography (GPC) characterization.

The molecular weight distribution and polydispersity of the azobenzene oligomers were determined using a GPC KF-806L column (Shodex) and an Ultimate 3000 auto sampler (Thermo), with THF as the eluent at 40 °C. Polystyrene (Shodex standard SM-105) was used as the molecular

weight standard. The number averaged molecular weight (M_n) of the azo-prepolymers was calculated using the following equation:

$$M_{n} = \frac{\Sigma N_{i} M_{i}}{\Sigma N_{i}}$$

where N_i is the intensity of the refraction response of each step, and M_i is the corresponding molecular weight. The weight averaged molecular weight is calculated via

$$M_{w} = \frac{\Sigma N_{i} M_{i}^{2}}{\Sigma N_{i} M_{i}}$$

and the polydispersity index (DPI) is calculated as M_n/M_w .

• Polarized optical microscopy (POM).

The occurrence of film alignment under strain is confirmed by measuring birefringence in crosspolarized optical microscopy (BX51P, Olympus).

• Photothermal analysis

The photothermal effect was monitored using a thermographic camera (FLIR-E30, FLIR).

• Mechanical analysis.

Thermomechanical analysis of the polymerized film was conducted on a DMA Q800 (TA Instruments). The storage modulus (E') and glass transition temperature (T_g) were measured at a frequency of 1 Hz with temperature ramping (-40 to 60 °C, 3 °C/min). The rubbery modulus (E_r) was determined from the measured storage modulus at $T_g + 10$ °C. The stress-strain relationship was measured under a strain-ramping model at 2%/min. The crosslinking density was calculated from the famous Flory's rubbery theory, following the equation:

$$v_e = \frac{E_r}{3RT_r}$$

where $T_r = T_g + 10$ °C is the starting temperature for the rubbery region, and R is the ideal gas constant.

• Photo-actuation characterization.

The samples for testing the photogenerated strain ($\Delta L/L_0$) were prepared by cutting the freestanding elastomer films into strips (15 mm × 8 mm). After loading with controlled force on the DMA, the samples were allowed to relax for 20 min before any photo-irradiation at room temperature. Collimated 365 and 530 nm light-emitting diodes (LEDs) (LCS-0365 and LCS-530, Mightex) were used to initiate and recover the photoisomerization of azobenzene. In a typical procedure, the relaxed film was first exposed to 365 nm irradiation (15 mW/cm²) for 10 min and then recovered by 530 nm irradiation (80 mW/cm²) for 10 min. Generally, this procedure was repeated for 5 times for each measured external force. The actuator specific work capacity was calculated through the equation:

$$\delta W = \frac{\Delta L}{L_0} \cdot \sigma_{\text{load}}$$

where ΔL is the measured length change, L_0 is the equilibrium length after applying the external load (σ_{load}). The power density output was calculated using the equation

$$P = \frac{d\Delta L}{dt} \cdot \frac{\sigma_{\text{load}}}{\rho}$$

where $\frac{d\Delta L}{dt}$ is the length change during each measured time step and ρ is the density of the synthesized polymer.

4. ¹H-NMR spectra of the synthesized compounds



Figure S1. 500MHz ¹H-NMR spectrum of 4-(4-hydroxy-phenylazo)benzoic acid (5 wt% in THF*d*₈)



Figure S2. 500MHz ¹H-NMR spectrum of 4-((4-(allyloxy)phenyl)diazenyl)benzoic acid (5 wt% in chloroform-*d*).



Figure S3. 500MHz ¹H-NMR spectrum of 3-hydroxypropyl 4-((4-(allyloxy)phenyl) diazenyl)benzoate (5 wt% in chloroform-*d*).



Figure S4. 500MHz ¹H-NMR spectrum of 3-(acryloyloxy)propyl 4-((4-(allyloxy) phenyl)diazenyl)benzoate (5 wt% in chloroform-*d*).



Figure S5. 500MHz ¹H-NMR spectrum of 3-hydroxypropyl 4-((4-(3-hydroxypropoxy)phenyl)diazenyl)benzoate (5 wt% in chloroform-*d*).



Figure S6. 500MHz ¹H-NMR spectrum of 3-(acryloyloxy)propyl 4-((4-(3-(acryloyloxy) propoxy)phenyl)diazenyl)benzoate (DA-azo) (5 wt% in chloroform-*d*).



Figure S7. 500MHz ¹H-NMR spectrum of 4-allyloxyphenyl-4-allyloxybenzoate (5 wt% in chloroform-*d*).

5. UV-VIS spectra



Figure S8. UV-VIS spectra of the (a) APAB-thiol thin film (75 μm) and (b) photo-isomerization of DA-azo (1M) in chloroform. The thin film contains APAB (50 mol%), ethanedithiol (EDT) (10 mol%) and pentaerythritol tetrakis(3-mercaptopropionate) PETMP (20 mol%) with an additional 1 mol% of DTBP and polymerized at 100 °C for 3 h and 130 °C for 12 h. For the isomerization measurement, 2 mW cm⁻² UV (365 nm) light was irradiated on the liquid cell via an optical fiber placed in the UV-VIS spectrometer. Spectra were collected after every 5 s of irradiation.

6. FTIR characterization



Figure S9. Kinetic profiles of acrylate conversion during thiol-Michael reaction in the presence of three different amine catalysts: TEA, DPA and DBU. Each monomer mixture contains (a) equal amounts of EDT and AB-azo (both 1 mol L⁻¹) or (b) 0.5 mol L⁻¹ of PETMP and 1 mol L⁻¹ of AB-azo in toluene. The catalyst was added right before the test. The dashed line indicates the measured IR data collected every 20 s.

7. Gel permeation chromatography (GPC) characterization



Figure S10. (a) (b) GPC traces of HeAB_M monomer mixture catalyzed by DBU, DPA and TEA. (b) GPC traces of the tested reaction cases after the thiol-Michael reaction (first step). To avoid any possible free radical generation, thermal initiators were not added. After the reaction, the solids formed at room temperature were dissolved in THF (0.5 wt%) for characterization.

8. POM characterization



Figure S11. POM images of HeAB_M azo-ICPRPs. The polarizers were set to 45° with respect to the stretching direction.

9. Mechanical characterization of HeAB_M and RAND samples



Figure S12. (a) Elastic properties of 2-step polymerized azo-ICPRPs and random polymers. (b) Thermo-mechanical properties of 2-step polymerized azo-ICPRPs and random polymers. RAND samples were prepared with identical monomer compositions and procedures as HeAB_M samples but without the addition of DBU.

10. Photo-thermal characterization



Figure S13. (a) Experimental setup for the photo-irradiation. (b-c) Thermal image of the azo-ICPRPs (HeAB_M) under the different intensity of UV irradiation (0 to 45 mW cm⁻²). (f) Relationship between the irradiation intensity and measured sample temperature after 15 minutes of irradiation.



11. Photo-strain responses of the synthesized azo-**ICPRPs** thin films

Figure S14. Photo-strain responses of the synthesized random co-polymers (RAND) and azo-ICPRPs. The actuations were measured under 365 nm (15 mW cm⁻²) and 530 nm illumination (80 mW cm⁻²) alternating every 10 min (as indicated in the profile).

80

-0.10

-0.15

0

20 40 6 Irradiation Time (min)

20

-0.10

-0.15

0

20

40

Irradiation Time (min)

60

80

60