

Mechano-isomerization of Azobenzene

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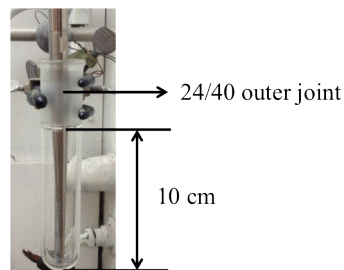
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General Experimental Methods. All reactions were carried out in oven-dried glassware (160 °C). The chemicals were purchased from major chemical suppliers and were used without further purification unless otherwise noted. Tetrahydrofuran (THF) was redistilled under argon atmosphere over sodium-benzophenone ketyl. All ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. Chloroform-D (CDCl_3) contained 0.05% v/v tetramethylsilane (TMS) and chloroform-D peak was set to 7.26 ppm on all proton spectra. Chemical shifts (δ) and coupling constants are reported in parts per million and Hertz, respectively. The abbreviations for splitting patterns are s, singlet; br s, broad singlet; d, doublet, t, triplet; q, quartet; and combinations therein (i.e. dd, doublet of doublets). Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry facility, which is supported, in part, by the National Science Foundation.

Gel permeation chromatography (GPC) was recorded in the NSF-sponsored Materials Research Science and Engineering Center on Polymers (MRSEC) at the University of Massachusetts Amherst. GPC analyses were performed on an Agilent 1260 tetrahydrofuran (THF) GPC with polystyrene as a standard and toluene as the flow rate marker and RI detection mode.

For photo/thermal isomerization and sonication studies, stock solutions of the polymer and monomer were prepared in Optima grade (Fischer) THF and acetonitrile. UV-Vis absorption spectra were measured using a Shimadzu UV 3600PC spectrometer. For photoisomerization studies, UV irradiation of the samples was carried out with a Model UVGL-25 equipped with a 365 nm, and light irradiation of the samples was carried out with a 26 W fluorescent light bulb.

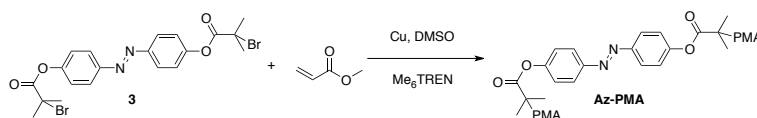
Ultrasound experiments were performed using Misonix Sonicator 3000 ultrasonic liquid processor operating at 20 kHz equipped with a 3.2 mm replaceable titanium probe. A Custom-made glass tube (see figure on right) was fabricated for sonication experiments by the glass shop at the



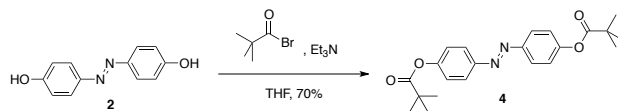
University of Massachusetts Amherst. The tube was placed in an ice bath, which was maintained at a temperature of 0-5 °C, as determined by a thermometer placed into the

ice bath. The entire sonication process was carried out in a dark room to prevent any photoisomerization. Pulsed (1.0 s on 0.5 s off) and continuous sonication was carried out at 12 W for each experiment.

Experimental Procedure:

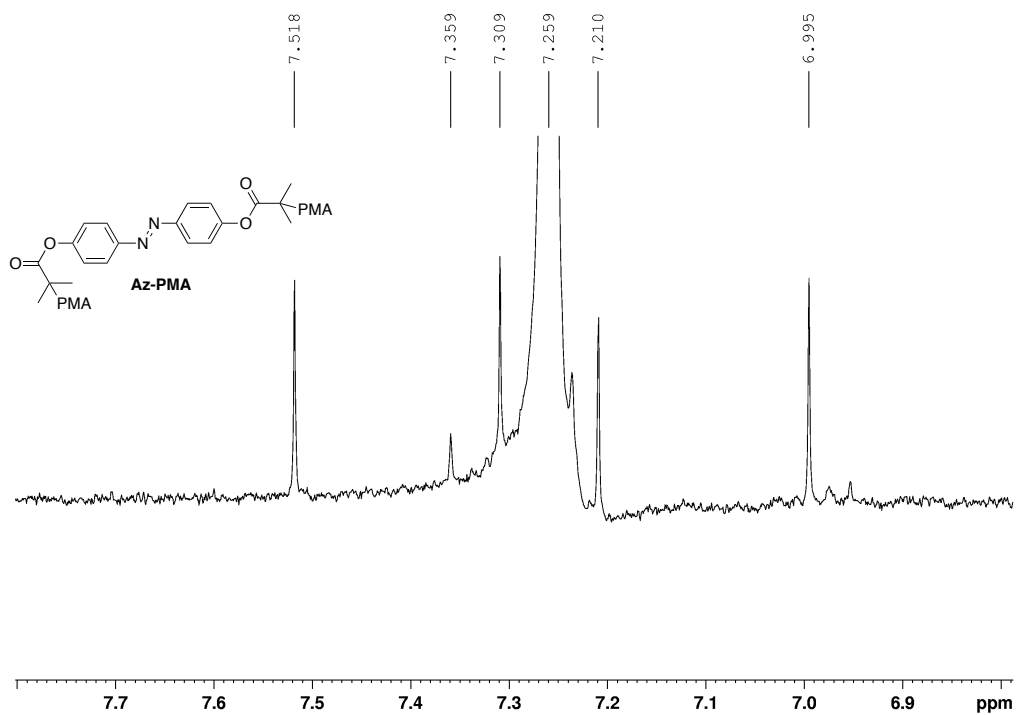
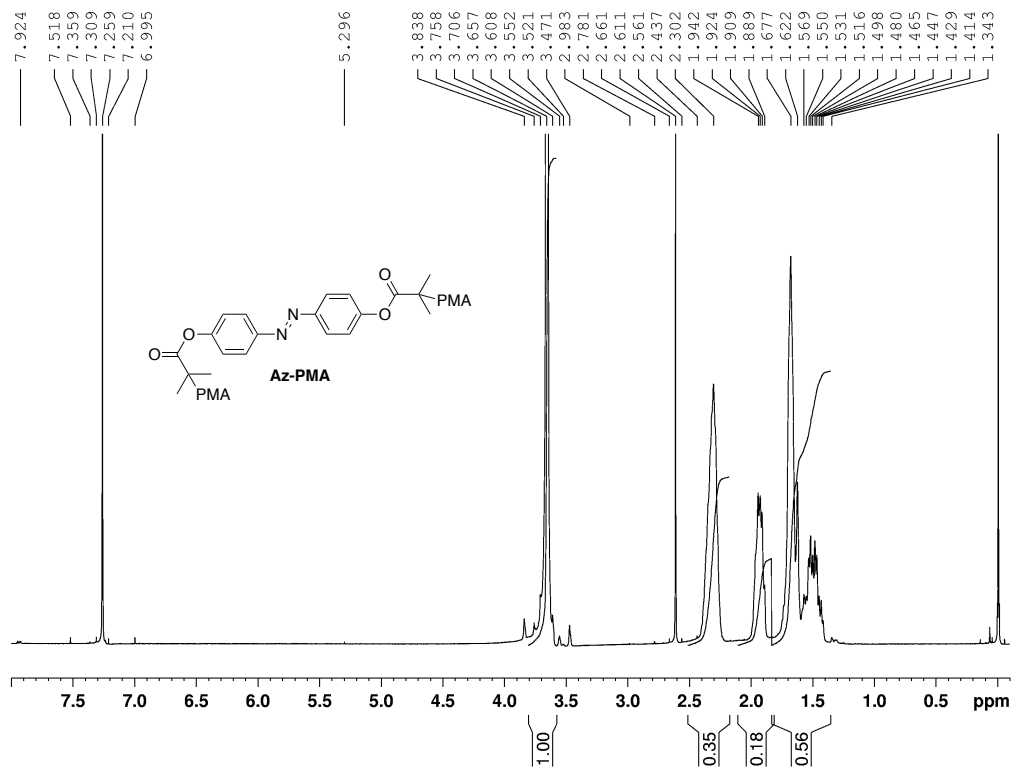


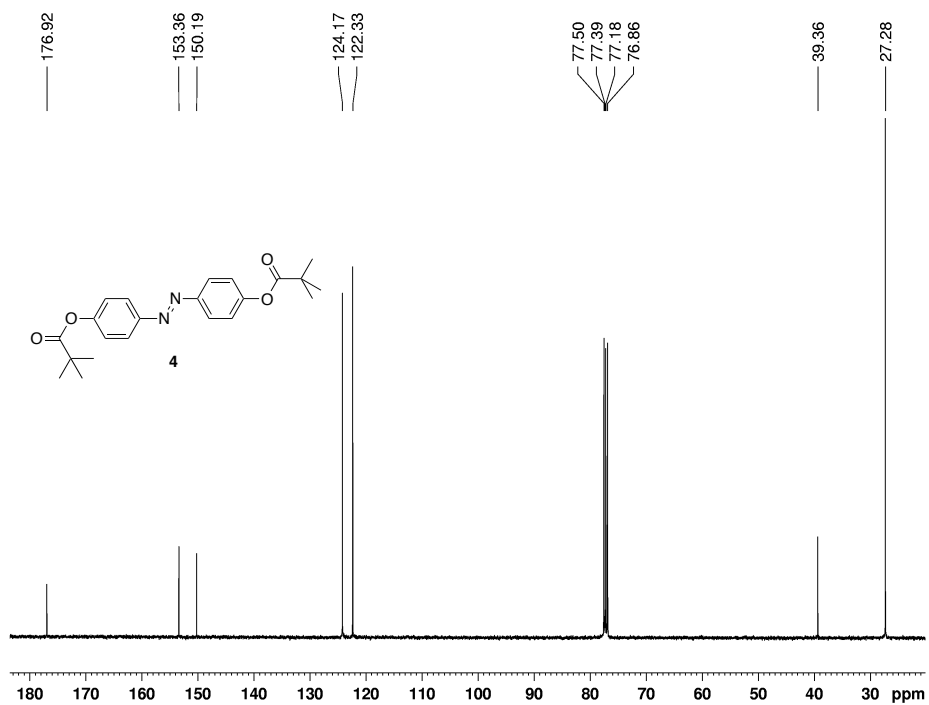
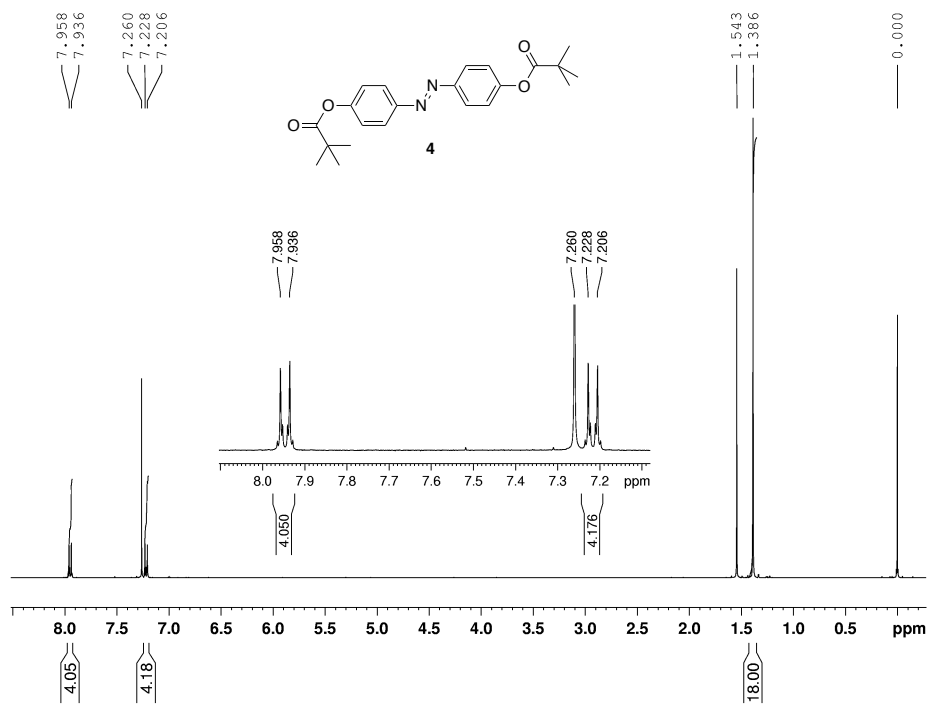
Az-PMA: In a 10 mL Schlenk flask containing a stir bar wound with copper wire (the copper wire was sanded before winding it around the stir bar), **3** (10.2 mg, 0.02 mmol), methyl acrylate (2 mL, 22.2 mmol), tris[2-(dimethylamino)ethyl]amine (0.026 mL, 0.1 M solution in DMSO), and DMSO (2 mL) were added under argon atmosphere and the mixture was subjected to three freeze pump thaw cycles. The reaction mixture was then stirred at room temperature for 17 h, after which the resulting polymer was collected by precipitation from methanol followed by filtration (975 mg, 51% yield). GPC: $M_n = 81$ kDa; $D = 1.4$.



4: In a 50 mL Schlenk flask **2** (270 mg, 1.26 mmol) was dissolved in dry THF (15 mL), to which triethylamine (0.53 mL, 3.8 mmol) was added under argon atmosphere and the reaction mixture cooled to -10 °C. To the above reaction mixture, a solution of pivaloyl bromide (0.47 mL, 3.8 mmol) in dry THF (5 mL) was added dropwise and the reaction mixture stirred at room temperature for 12 h. The reaction mixture was then filtered, the solvent removed under vacuum to obtain a yellowish orange color solid. This solid was dissolved in chloroform and extracted three times with nanopure water. The combined chloroform extracts were dried over Na_2SO_4 , filtered and the solvent removed under vacuum to obtain crude **4**, which was purified by recrystallization in ethanol to obtain orange crystals of **4** (300 mg, 63% yield). ^1H NMR (CDCl_3 , 400 MHz) δ 1.39 (s, 18H), 7.22 (d, $J = 8.87$ Hz, 4H), 7.95 (d, $J = 8.92$ Hz, 4H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 27.28, 39.36, 122.33, 124.17, 150.19, 153.36, 176.62; HRMS (ESI) m/z For $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_4$

$[M + H]^+$ calculated 383.1893, found 383.1942.





General Procedure for Photoisomerization Studies: In a vial a solution of **Az-PMA** (3 mg/mL) in THF was taken and the UV-vis spectra recorded (labeled as parent in figure S1). The vial was then capped and sealed with a parafilm and exposed to UV light at $\lambda=365$ nm for an hour after which, the UV-vis spectra of the UV irradiated sample was recorded in dark (labeled as UV in figure S1). The UV irradiated sample was then exposed to light from a 26 W fluorescent light bulb for two hours and the UV-vis spectra recorded (labeled as light in figure S1). The procedure was also repeated for the photoisomerization study of **4** (1 mM) in THF (figure S1b).

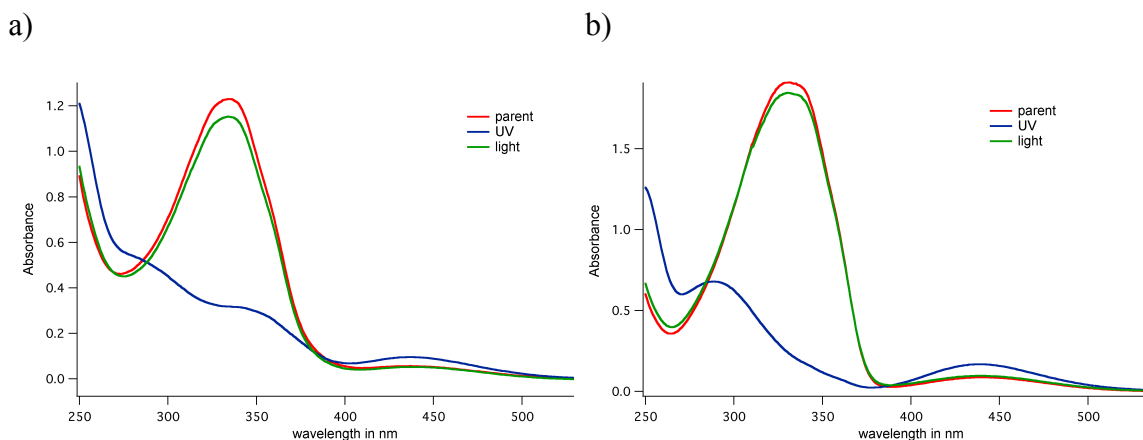


Fig. S1 Photoisomerization of a) **Az-PMA** (3 mg/mL) in THF and b) **4** (0.1 mM) in THF.

General Procedure for Pulsed Sonication Experiments: In a flask a stock solution of **Az-PMA** (1 mg/mL) in THF (45 mL) was prepared, from which four samples of 10 mL each was transferred into five separate vials. The remaining 5 mL stock solution was used to record the UV-vis spectra (parent). Each vial was then exposed to UV light at $\lambda=365$ nm for an hour after which, the UV-vis spectra of the UV irradiated sample was recorded in dark (labeled as UV in figure 1). 8 mL of UV irradiated solution from each vial was transferred into the sonication glass tube placed in an ice bath (0-5 °C) and subjected to pulsed (1 s on and 0.5 s off) sonication at 12 W in dark. Each sample was sonicated for a different duration of time, starting with 30 minutes for the first sample. Subsequent samples were sonicated for 60, 90 and 120 minutes. After sonication, the volume of the entire sonicated solution was measured in a graduated cylinder to ensure that no solvent had evaporated during the sonication process and the volume of solution after sonication

for each batch measured 8 mL. The UV-vis spectra (recorded in dark) and GPC for each sonicated sample was recorded. The 120 min sonicated sample was exposed to light from a 26 W fluorescent light bulb for 2 h and the UV-vis spectra recorded.

4: 0.1 mM solution of **4** in THF was used for the pulsed sonication experiment of **4** (figure 2).

General Procedure for Continuous Sonication Experiments: Continuous sonication at 12 W was carried out for **Az-PMA** (45 mL of 1mg/mL) and **4** (0.1 mM) in THF, keeping the same procedure and sonication times as that of the pulsed sonication experiment (figure S2a and S2b).

Procedure for Pulsed Sonication in Acetonitrile: The above procedure (for pulsed sonication in THF) was utilized for pulsed sonication of **Az-PMA** (45 mL of 1mg/mL) and **4** (0.1 mM) in acetonitrile at 12 W (figure S3a and S3b). Each batch of **Az-PMA** solution in acetonitrile after sonication for the specified time was subjected to vacuum, and the sonication product redissolved in THF to record the GPC.

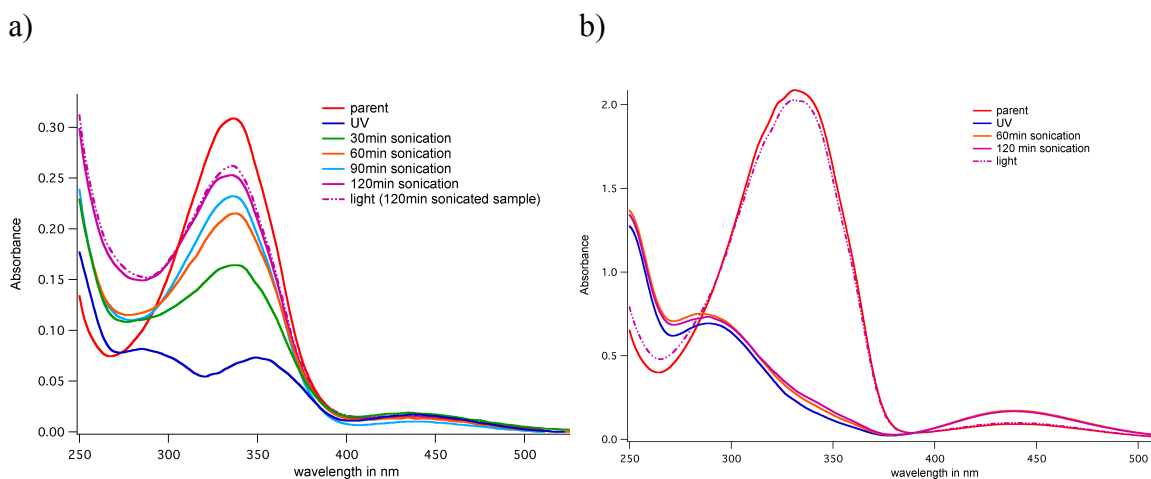


Fig. S2 UV-vis spectra of a) *cis*-Az-PMA (1 mg/mL) in THF with increase in continuous sonication time and subsequent exposure to light from a 26 W fluorescent light bulb and b) *cis*-4 (0.1 mM) in THF upon sonication for 60 and 120 minutes, and subsequent exposure to light from a 26 W fluorescent light bulb (120 minutes sonicated solution). The red curve in both the figures corresponds to parent *trans*-Az-PMA (a) and *trans*-4 (b). The blue curve in both the figures corresponds to UV irradiated *cis*-Az-PMA (a) and *cis*-4 (b).

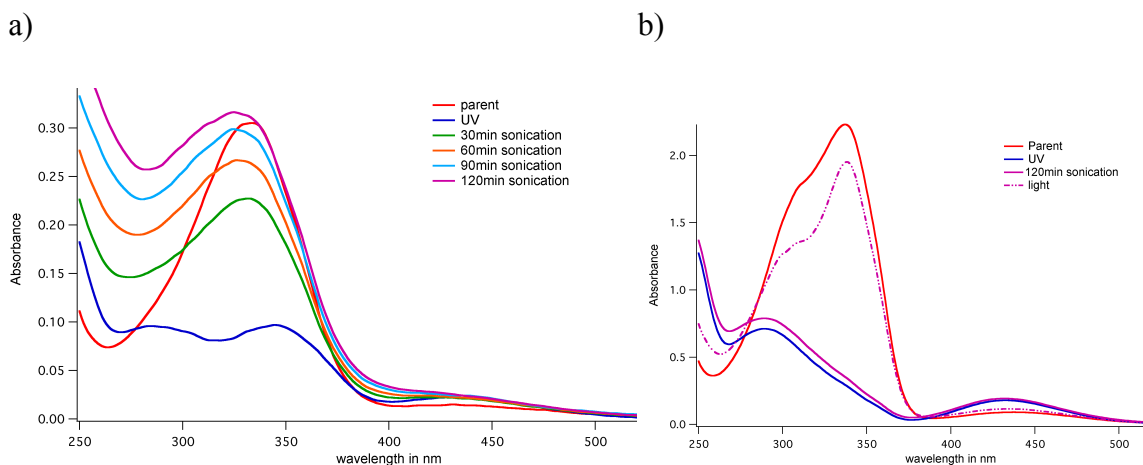


Fig. S3 UV-vis spectra of a) *cis*-Az-PMA (1 mg/mL) in acetonitrile with increase in pulsed sonication time and b) *cis*-4 (0.1 mM) in acetonitrile upon sonication for 120 minutes, and subsequent exposure to light from a 26 W fluorescent light bulb (120 minutes sonicated solution). The red curve in both the figures corresponds to parent *trans*-Az-PMA (a) and *trans*-4 (b). The blue curve in both the figures corresponds to UV irradiated *cis*-Az-PMA (a) and *cis*-4 (b).

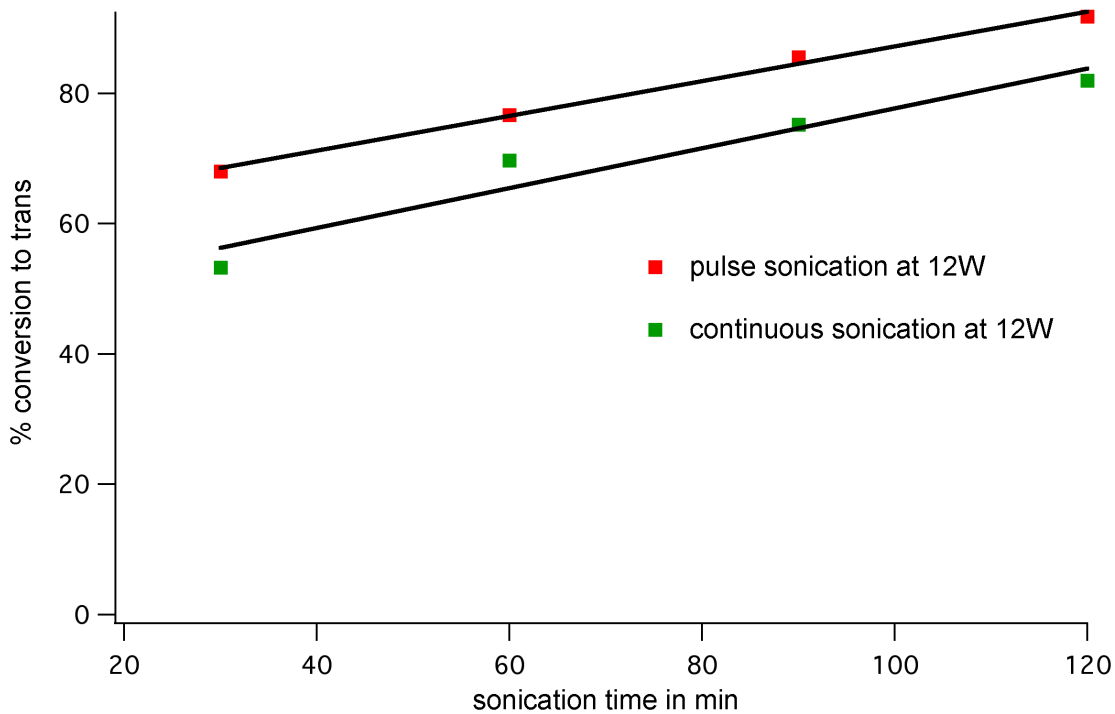


Fig. S4 Difference in percentage of conversion from *cis*-Az-PMA \rightarrow *trans*-Az-PMA with increase in sonication time by pulse and continuous method in THF at 12 W, and 0-5 °C.

GPC:

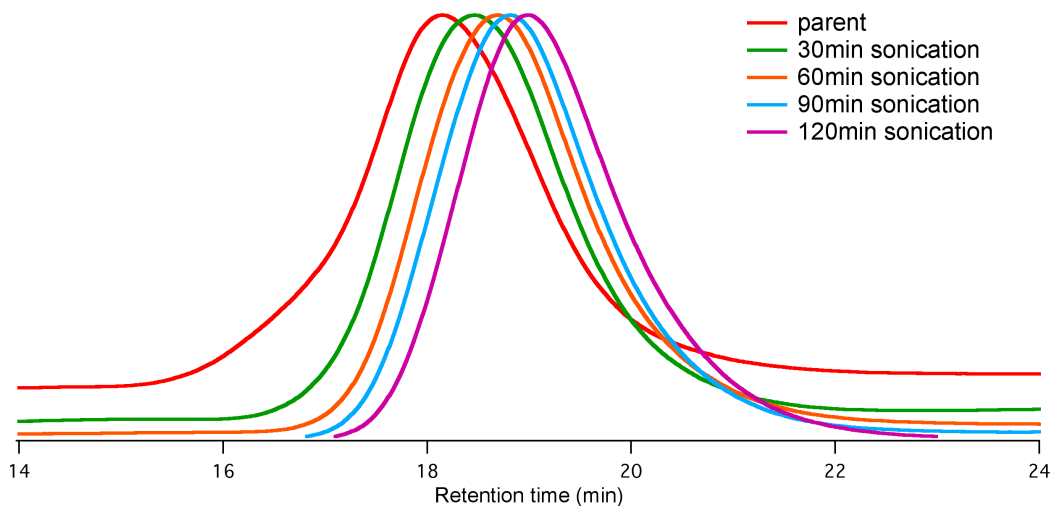


Fig. S5 Normalized GPC curves of **Az-PMA** in THF with increase in pulsed sonication time (30-120 min) in THF at 12 W, and 0-5 °C.

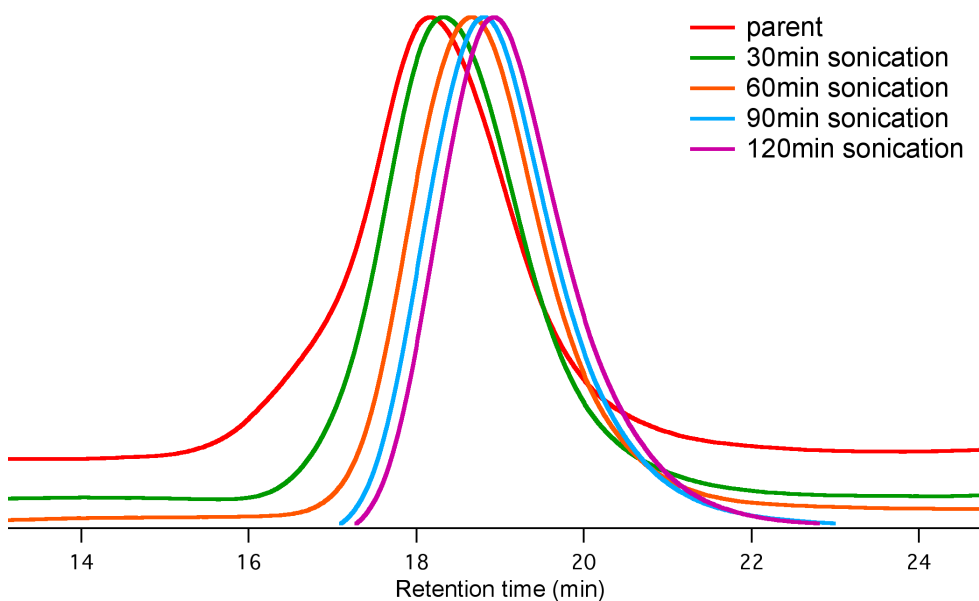


Fig. S6 Normalized GPC curves of **Az-PMA** in THF with increase in continuous sonication time (30-120 min) in THF at 12 W, and 0-5 °C.

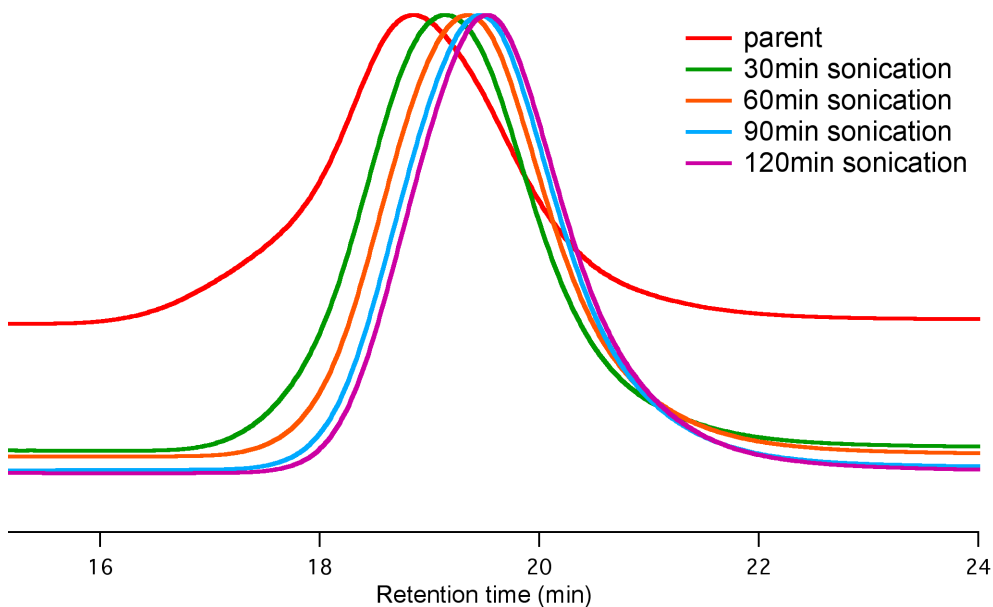


Fig. S7 Normalized GPC curves of **Az-PMA** in THF with increase in pulsed sonication time (30-120 min) in acetonitrile at 12 W, and 0-5 °C.

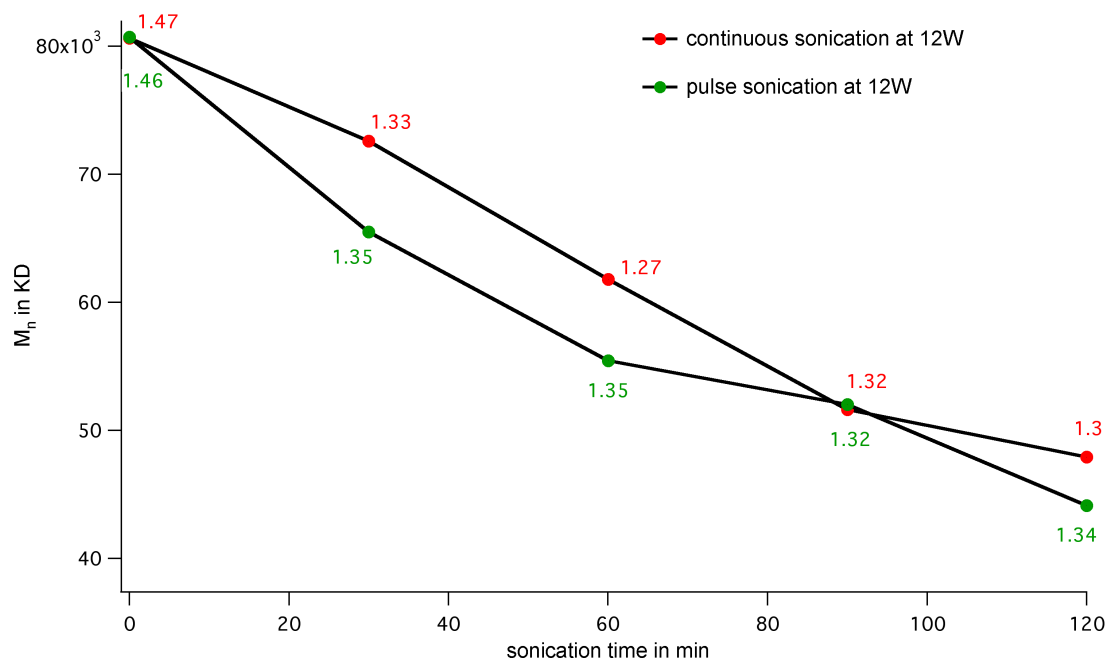


Fig. S8 Comparison of decrease in M_n (kDa) of **Az-PMA** when subjected to sonication by pulse and continuous method in THF at 12W, and 0-5 °C. The values indicated next to each data point corresponds to the polydispersity index (D) of the polymer.

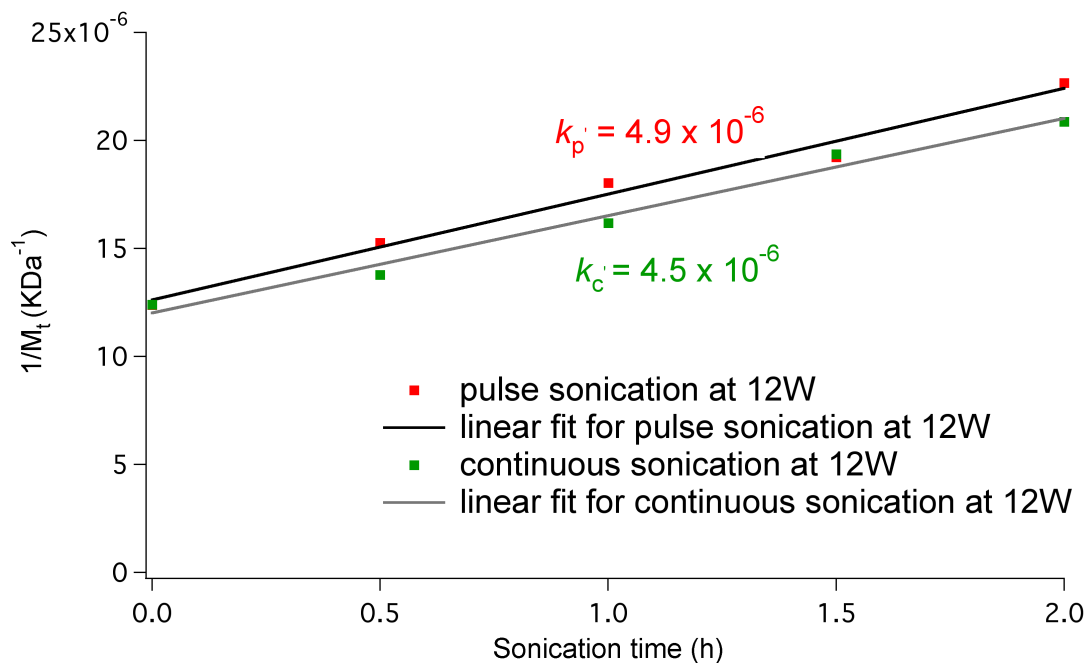
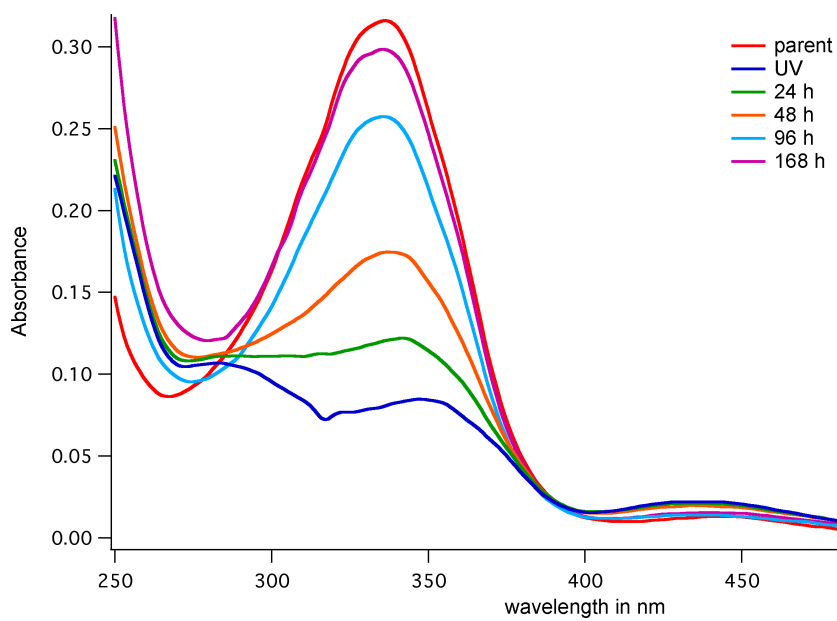


Fig. S9 Reciprocal of number average molecular weight ($1/M_n$) of **Az-PMA** at sonication time t vs sonication time in minutes, and best linear fit to equation (1) with an intercept of $1/M_i$ for pulsed and continuous sonication at 12 W in THF.

General Procedure for Thermal *cis*→*trans* Isomerization Studies: In a vial a solution of **Az-PMA** (10 mL of 1 mg/mL) in THF was taken and the UV-vis spectra recorded (labeled as parent in figure S9). The vial was then capped and sealed with a parafilm and exposed to UV light at $\lambda=365$ nm for an hour after which, the UV-vis spectra of the UV irradiated sample was recorded in dark (labeled as UV in figure S9). The vial was then sealed and wrapped completely in an aluminum foil and placed in dark. Periodically (every 24 h) over a week, 1 mL of sample was taken from the vial to record the UV-vis spectra (done in dark).

4: 0.52 mM solution of **4** in THF was used for thermal *cis*→*trans* isomerization studies by employing the above procedure.

a)



b)

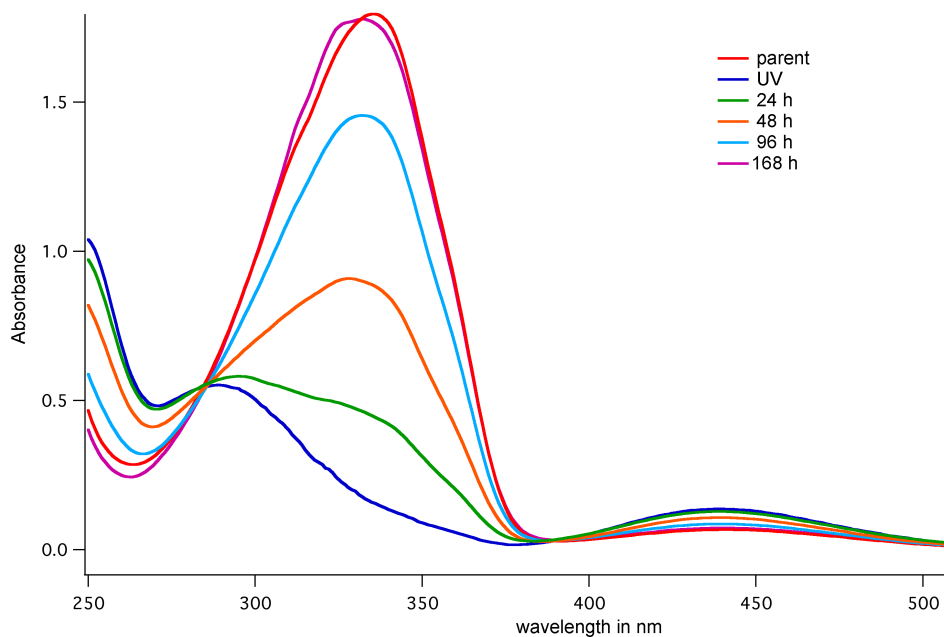
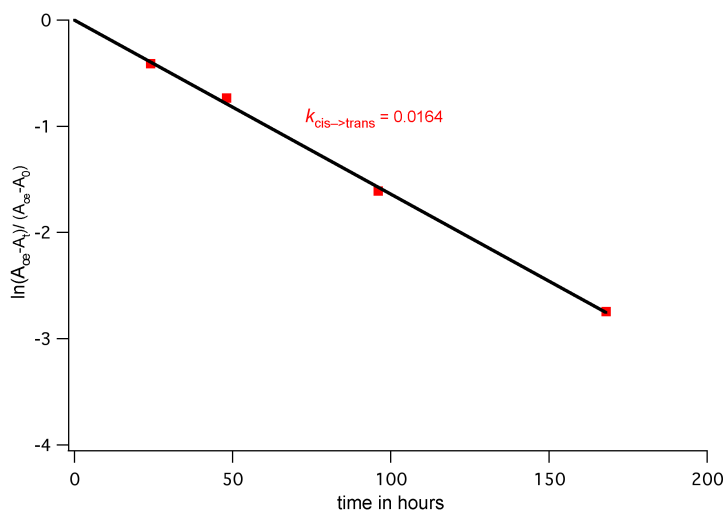


Fig. S10 UV-vis spectra showing a) thermal isomerization of *cis*-Az-PMA \rightarrow *trans*-Az-PMA in THF (1 mg/mL) at room temperature in dark over a period of 168 h and b) thermal isomerization of *cis*-4 \rightarrow *trans*-4 in THF (0.52 mM) at room temperature in dark over a period of 168 h.

First Order Kinetic Plots for Thermal *cis*→*trans* Isomerization of Az-PMA and 4:

The first order rate constants for thermal *cis*→*trans* isomerization ($k_{cis \rightarrow trans}$) of Az-PMA and 4 (figure S10) were obtained by fitting the change in absorbance (see figure S9) of the samples to equation (2), (shown in the main text of the paper).

a)



b)

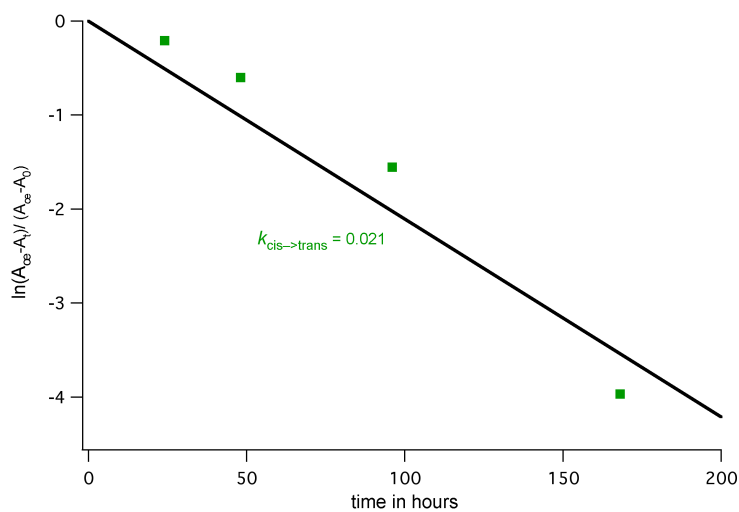


Fig. S11 First order kinetic plots and rate constants ($k_{cis \rightarrow trans}$) for thermal *cis*→*trans* isomerization of a) Az-PMA and b) 4.

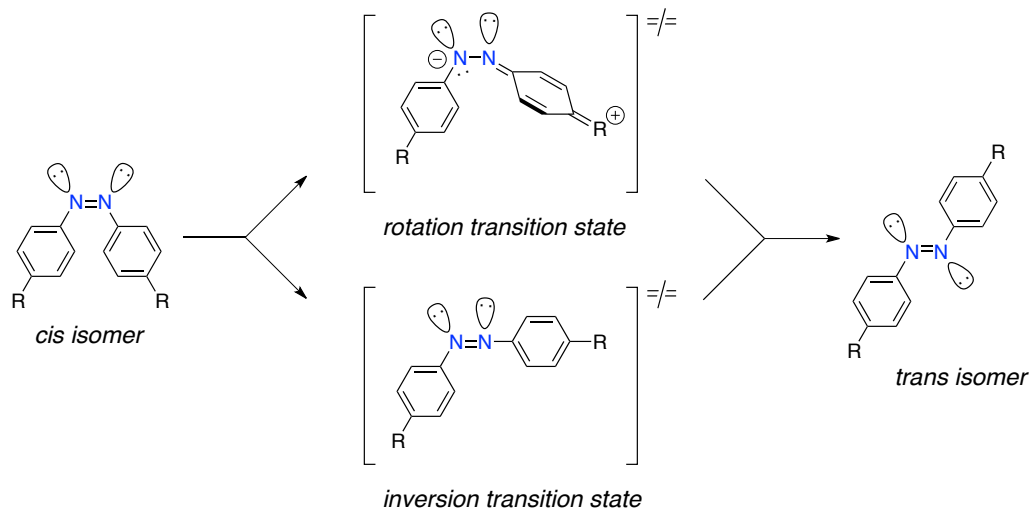


Fig. S12 Proposed rotation and inversion mechanism for the *cis* to *trans* isomerization of azobenzene

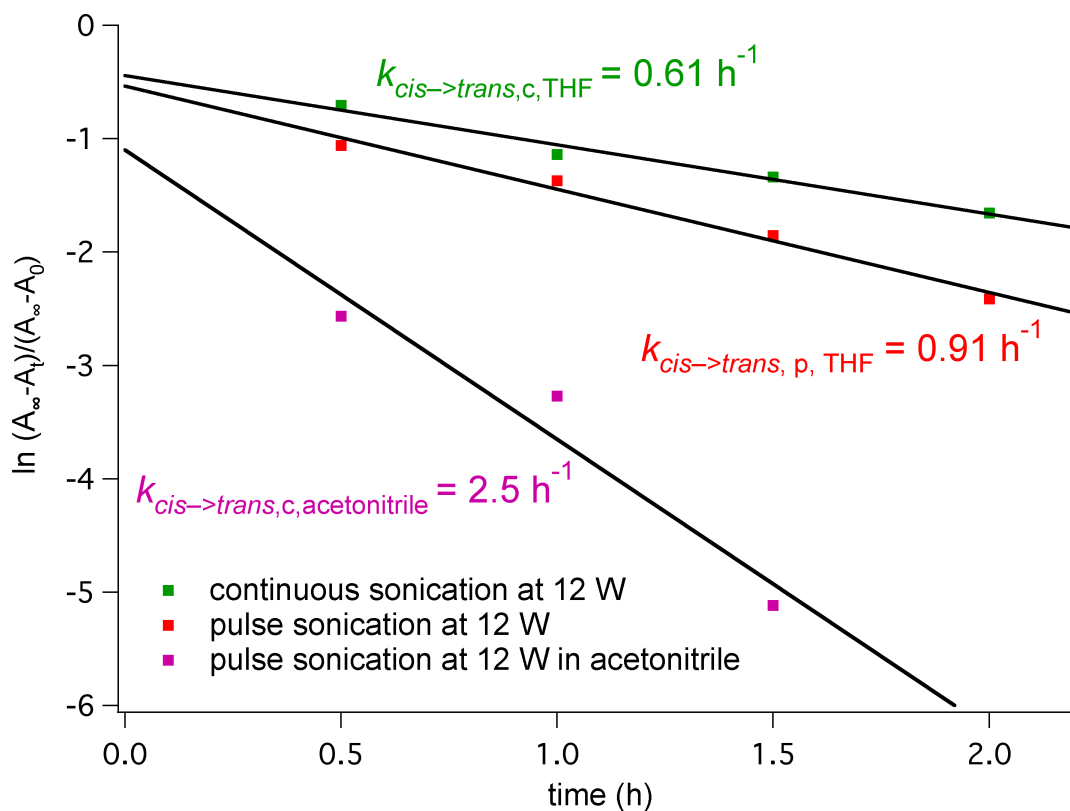


Fig. S13 Approximate first order rate constants for the *cis* to *trans* mechanoisomerization of Az-PMA in THF and acetonitrile.