Supporting Information for

Is Molecular Weight or Degree of Polymerization a Better Descriptor of Ultrasound-Induced Mechanochemical Transduction?

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I. General Experimental Details

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without purification. Anhydrous acetonitrile was obtained from Acros (Acroseal, 99.9%). Methyl ethyl ketone (MEK), Cu(0) powder (99%, 1–5 μm) and Me_6TREN were purchased from Sigma-Aldrich. Silica gel 60 (230–400 mesh) was purchased from Silicycle. Acrylate monomers were filtered through basic alumina to remove the inhibitors prior to use and kept under an argon atmosphere. Cu(0) powder was sonicated in DMSO in a Fisher Scientific Tabletop Ultrasonic Cleaner, model FS-20D (0.75 gal tank), 40 kHz, with a max input power of 80 W. All synthetic reactions and sonication experiments were performed under argon atmosphere.

Analytical gel permeation chromatograph (GPC) analyses were performed with a Waters1515 Isocratic HPLC pump, a Waters (2998) Photodiode Array Detector, a Waters (2414) Refractive Index Detector, a Waters (2707) 96-well autosampler, and a series of 4 Waters HR Styragel columns (7.8 x 300mm, HR1, HR3, HR4, and HR5) in THF at 30 °C. The GPC was calibrated using monodisperse polystyrene standards. UV-Vis spectra were recorded using a Shimadzu UV-2401PC. Standard quartz cells and standard quartz flow cell cuvettes with a path length of 10 mm were purchased from Starna Cells. UV irradiation of samples dissolved in acetonitrile or MEK was performed with a Model UVG-11 Mineralight lamp (short wave UV-254 nm or long wave UV-365 nm).

Ultrasound experiments were performed on a Vibra Cell 505 liquid processor with a ½″ diameter solid probe from Sonics and Materials. The distance between the titanium tip and bottom of the Suslick cell was 1 cm. The Suslick cells were made by the School of Chemical Sciences Glass Shop at the University of Illinois. PTFE tubing was used to circulate the solution. A peristaltic pump equipped with a Masterflex L/S PTFE-tubing pump head was purchased from

Cole-Parmer. A Neslab CC 100 immersion cooler equipped with a Neslab cryotrol temperature controller was used to maintain the temperature of a cooling bath.

II. Control Experiments

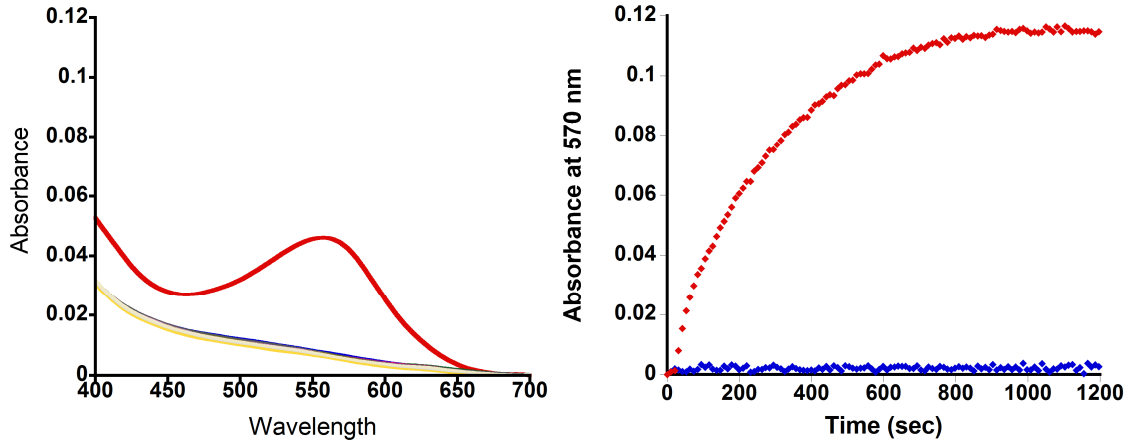


Figure S1. (*left*) UV-vis absorption spectra acquired during ultrasonication of PMA control polymer containing spiropyran at the chain-end and after activation by 365 nm UV light (red curve). A total of 15 spectra were collected at 2 minute intervals for 30 min of sonication with no change in absorption observed. (*right*) Absorbance at 570 nm during ultrasound irradiation of 156 kDa PMA (red trace) and 154 kDa PMA control polymer (blue trace).

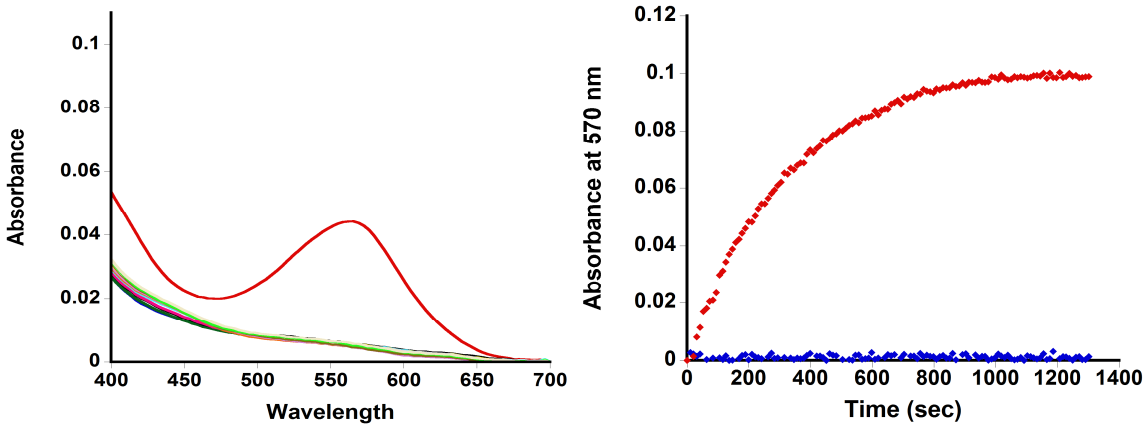


Figure S2. (*left*) UV-vis absorption spectra acquired during ultrasonication of PEA control polymer containing spiropyran at the chain-end and after activation by 365 nm UV light (red curve). A total of 15 spectra were collected at 2 minute intervals for 30 min of sonication with no change in absorption observed. (*right*) Absorbance at 570 nm during ultrasound irradiation of 177 kDa PEA (red trace) and 166 kDa PEA control polymer (blue trace).

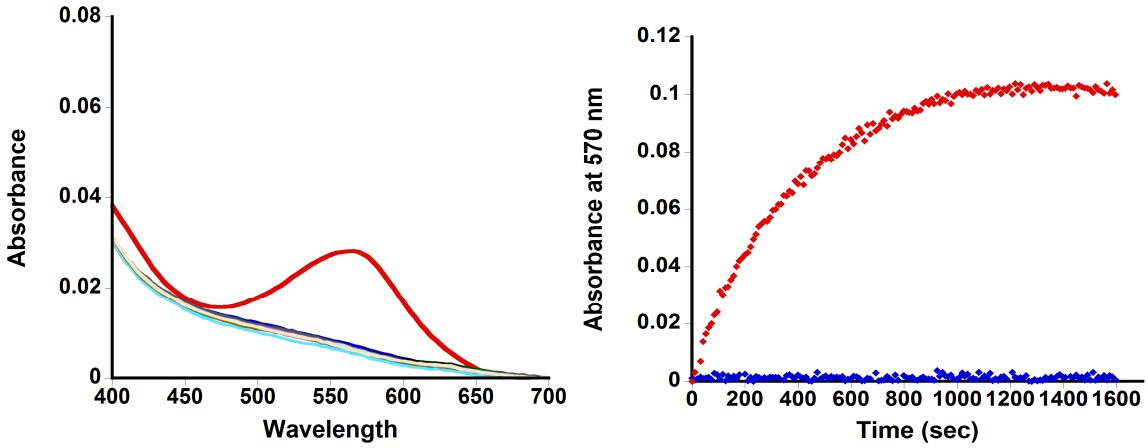


Figure S3. (*left*) UV-vis absorption spectra acquired during ultrasonication of PnBA control polymer containing spiropyran at the chain-end and after activation by 365 nm UV light (red curve). A total of 15 spectra were collected at 2 minute intervals for 30 min of sonication with no change in absorption observed. (*right*) Absorbance at 570 nm during ultrasound irradiation of 139 kDa PnBA (red trace) and 169 kDa PnBA control polymer (blue trace).

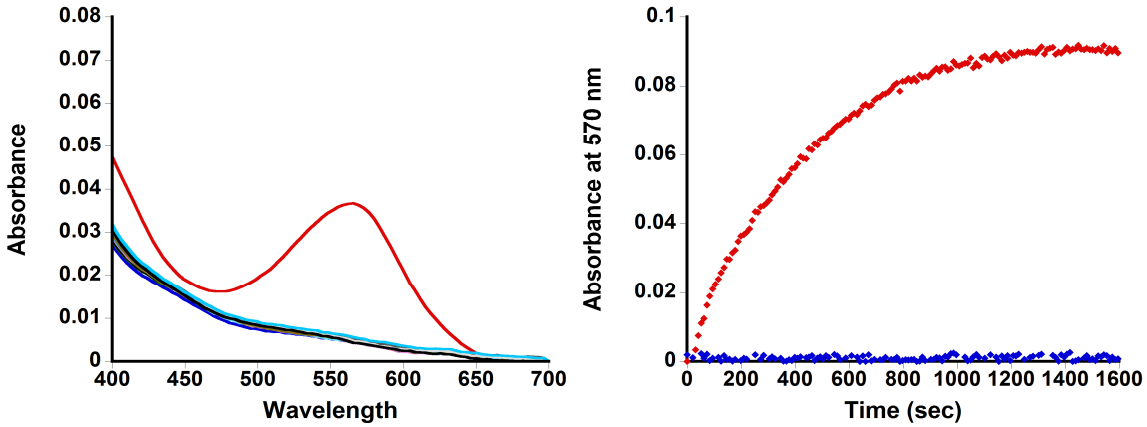


Figure S4. (*left*) UV-vis absorption spectra acquired during ultrasonication of PiBA control polymer containing spiropyran at the chain-end and after activation by 365 nm UV light (red curve). A total of 15 spectra were collected at 2 minute intervals for 30 min of sonication with no change in absorption observed. (*right*) Absorbance at 570 nm during ultrasound irradiation of 152 kDa PiBA (red trace) and 149 kDa PiBA control polymer (blue trace).

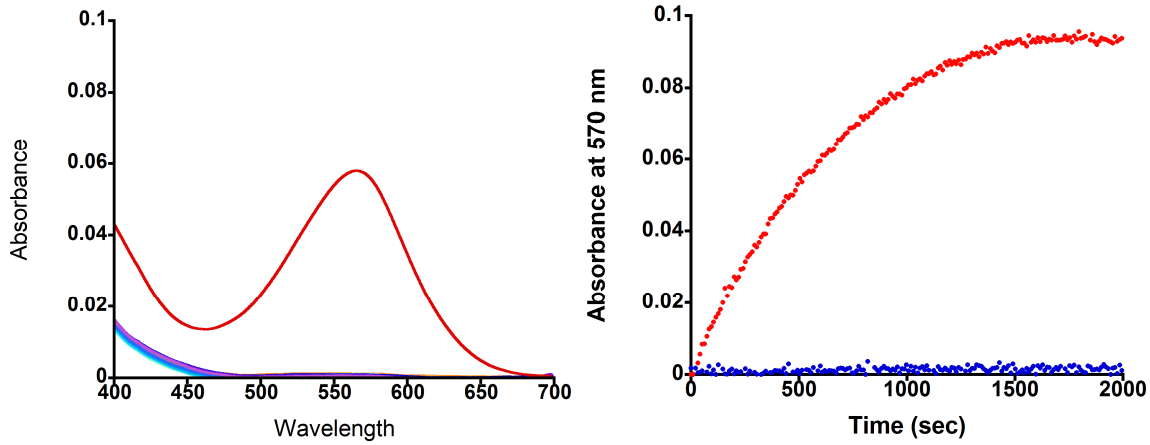


Figure S5. (*left*) UV-vis absorption spectra acquired during ultrasonication of PtBA control polymer containing spiropyran at the chain-end and after activation by 365 nm UV light (red curve). A total of 15 spectra were collected at 2 minute intervals for 30 min of sonication with no change in absorption observed. (*right*) Absorbance at 570 nm during ultrasound irradiation of 124 kDa PtBA (red trace) and 131 kDa PtBA control polymer (blue trace).

III. Thermal Reversion Experiments

The reverse ring closing reaction of the merocyanine to the closed spiropyran form was analyzed for all polymers. Polymers were irradiated with 365 nm UV light for 5 min to shift the equilibrium to the merocyanine photostationary state. These experiments were conducted in the flow cell system with the temperature matched to the sonication experiments in order to reproduce the conditions of the ultrasonication experiments as closely as possible. To achieve this, the acetone bath was maintained at 2 °C, which achieved a temperature of 3–5 °C in the Suslick cell. The rate of the reverse reaction was determined from the first order rate law (-dA/dt = k_{obs} A) in its logarithmic form:

$$ln\left(\frac{A_t - A_f}{A_0 - A_f}\right) = -k_r t \qquad \text{(S1)}$$

where A_0 and A_t are the absorbance at λ_{max} at 0 min and t min, respectively. A_f is the absorbance of the solution at λ_{max} before irradiation, and k_r is the observed rate constant for thermal

reversion. The calculated rate constants in MEK are displayed in Table S1. Thermal reversions for all polymer compositions were nearly identical, indicating that electronic contributions of the local polymer environment do not significantly influence the rate of activation. The reversion rate constants were also significantly slower than the forward ring-opening reaction and thus were not included in calculations of mechanochemical activation rate constants.

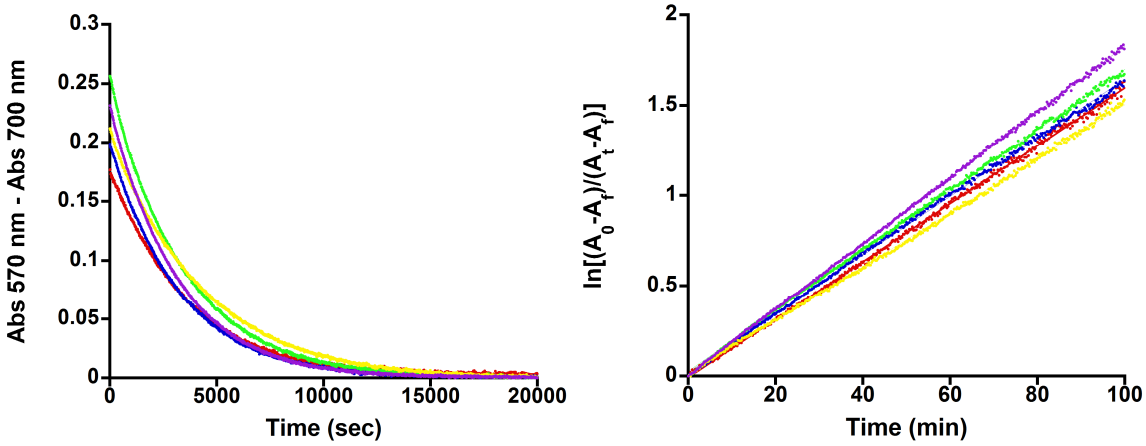


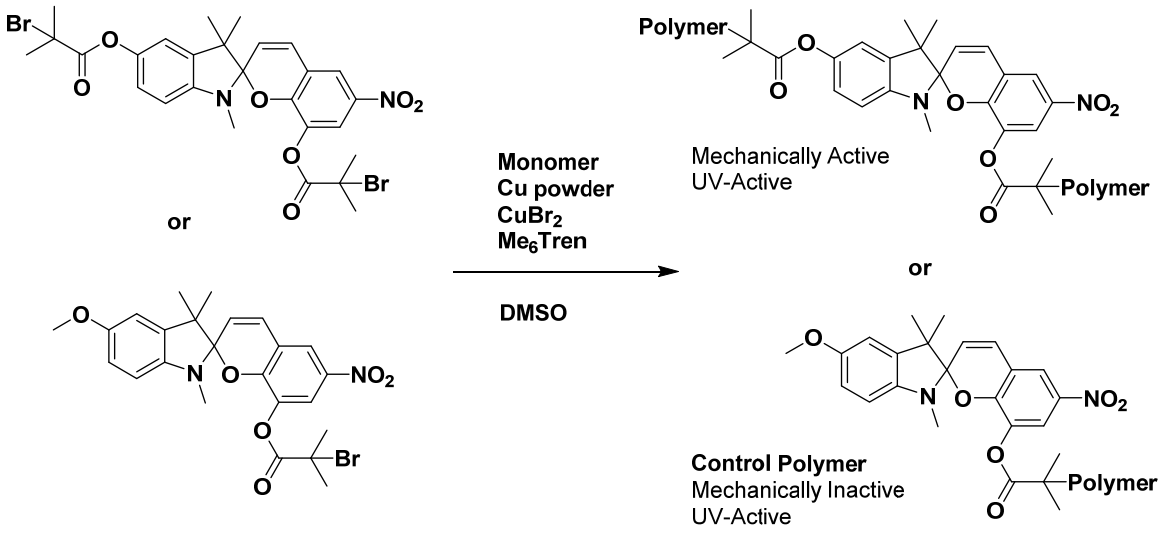
Figure S6. (*left*) Absorbance data for the reversion of merocyanine to spiropyran after activation with 365 nm UV light, and (*right*) rates of reversion calculated using first order kinetics with the slopes of the lines equal to k_r. 156 kDa PMA (red), 155 kDa PEA (blue), 137 kDa PnBA (green), 155 kDa PiBA (yellow), 131 kDa PtBA (purple).

Table S1: Measured rate constants (min^{-1}) of thermal reversion for PMA, PEA, PnBA, PiBA, and PtBA in MEK at 3–5 °C after activation of spiropyran with 365 nm UV light.

PMA		**PEA**		**PnBA**		**PiBA**		**PtBA**	
M_n (kDa)	**k_r**	**M_n (kDa)**	**k_r**	**M_n (kDa)**	**k_r**	**M_n (kDa)**	**k_r**	**M_n (kDa)**	**k_r**
156	0.016	155	0.016	137	0.017	155	0.015	131	0.018

IV. Synthetic Procedures

Scheme S1. Polymerization of various acrylate monomers from a bis-functional or mono-functional (control) spiropyran initiator.



General Procedure for Polymer Synthesis. Cu(0) (2.44 mg) was weighed using an analytical balance and then added to a 20 mL scintillation vial. DMSO (0.5 ml) was added to the vial and the mixture was sonicated in a sonication bath for c.a. 1 min. An aliquot of 0.25 mL (containing 1.22 mg Cu(0), 0.0192 mmol, 2 equiv) was removed and added to a 10 mL Schlenk flask equipped with a teflon stir bar. $CuBr_2$ (1.72 mg) was added to 2 mL of DMSO and allowed to dissolve. An aliquot of 0.25 mL was removed (containing 0.215 mg $CuBr_2$, 0.000961 mmol, 0.1 equiv) and added to the Schlenk flask. Me_6TREN (5.40 μL, 0.0202 mmol, 2.1 equiv) was measured with a microliter syringe and transferred to the Schlenk flask. Monomer (1.00 mL, 11.1 mmol, 1154 equiv) was added. Lastly, the initiator[1,2] (6.27 mg, 0.00961 mmol, 1 equiv) was added to the flask. The flask was immediately sealed with a ground glass stopper, secured with copper wire, and three freeze-pump-thaw cycles were applied to remove dissolved oxygen. The flask was backfilled with argon and was allowed to stir in a water bath for 2 h at room

temperature. The polymerization was opened to air, 10 mL of THF were added, and the polymer filtered through a pad of silica gel. After solvent was removed *in vacuo*, a concentrated mixture of polymer in THF was precipitated by dropwise addition to stirring cold methanol. Poly(ethyl acrylate), poly(n-butyl acrylate), poly(*iso*-butyl acrylate), and poly(*tert*-butyl acrylate) were precipitated from a 50:50 mixture of MeOH:H_2O. The resulting polymer was collected and dried under vacuum at 50 °C.

Table S2: Ratios of reagents used for polymer syntheses.

Polymer Type	Initiator (equiv)	Cu(0) (equiv)	$CuBr_2$ (equiv)	Me_6Tren (equiv)	DMSO (vol)	Monomer (vol)
PMA	1.0	2.0	0.1	2.1	0.5 ml	1.0 ml
PEA	1.0	2.0	0.1	2.1	0.5 ml	1.0 ml
PnBA	1.0	2.0	0.1	2.1	0.5 ml	1.0-1.5 ml
PiBA	1.0	2.0	0.1	2.1	0.5 ml	1.0-1.5 ml
PtBA	1.0	2.0	0.5	2.5	0.5 ml	1.0-1.5 ml

Table S3. Molecular weight and PDI data for synthesized polyacrylates.

PMA		PEA		PnBA		PiBA		PtBA	
M_n (kDa)	PDI	M_n (kDa)	PDI	M_n (kDa)	PDI	M_n (kDa)	PDI	M_n (kDa)	PDI
270	1.25	282	1.16	224	1.21	309	1.31	292	1.21
194	1.24	233	1.13	184	1.30	239	1.32	273	1.26
184	1.21	177	1.24	137	1.33	167	1.18	226	1.18
156	1.22	155	1.16	98	1.35	152	1.19	178	1.17
139	1.28	121	1.11	87	1.24	81	1.17	131	1.12
102	1.31	96	1.28	60	1.25	60	1.13	89	1.27
54	1.34	77	1.22					50	1.19
		49	1.22						

V. GPC Chromatograms

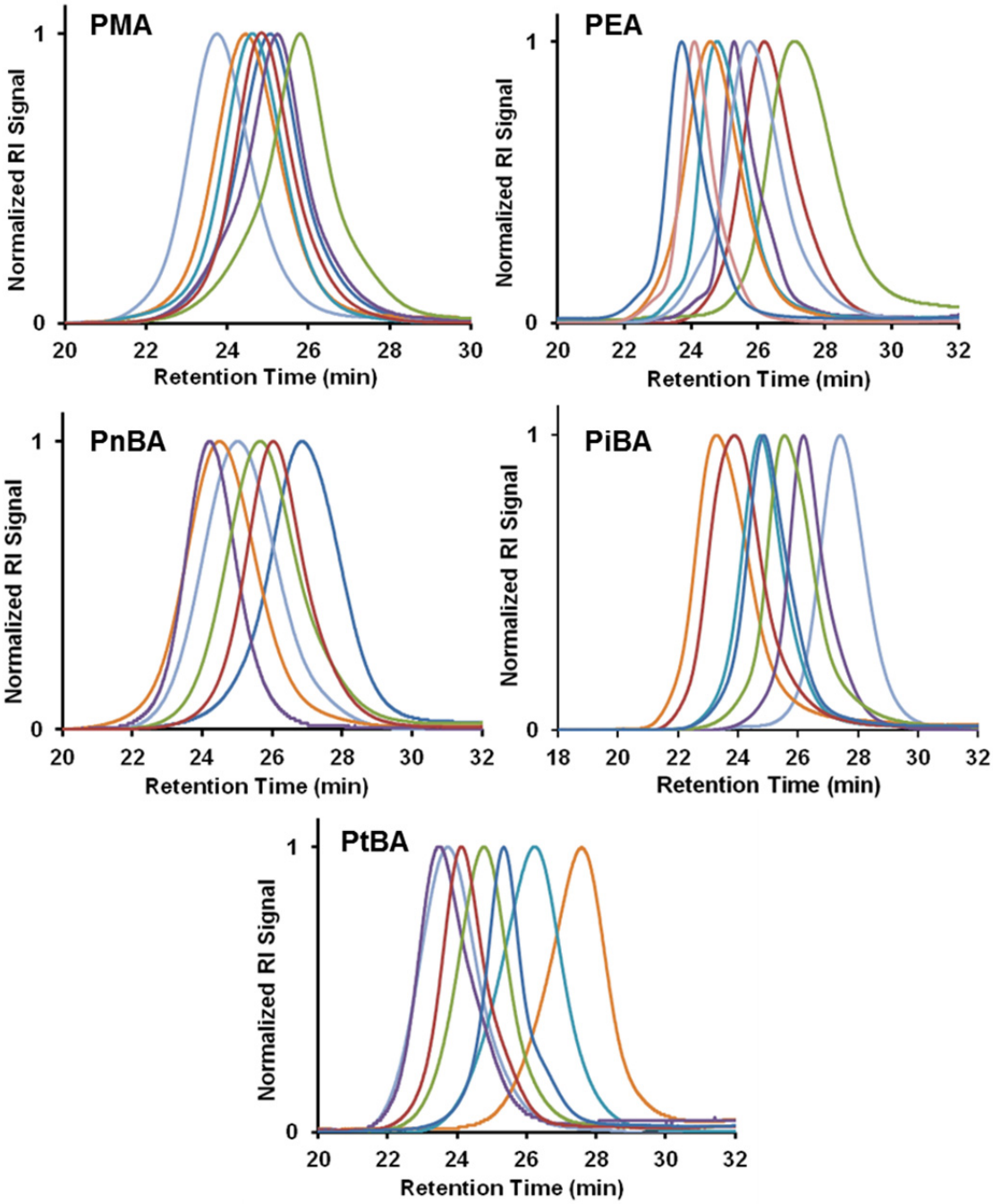


Figure S7. GPC traces of all polymers containing a chain-centered spiropyran mechanophore.

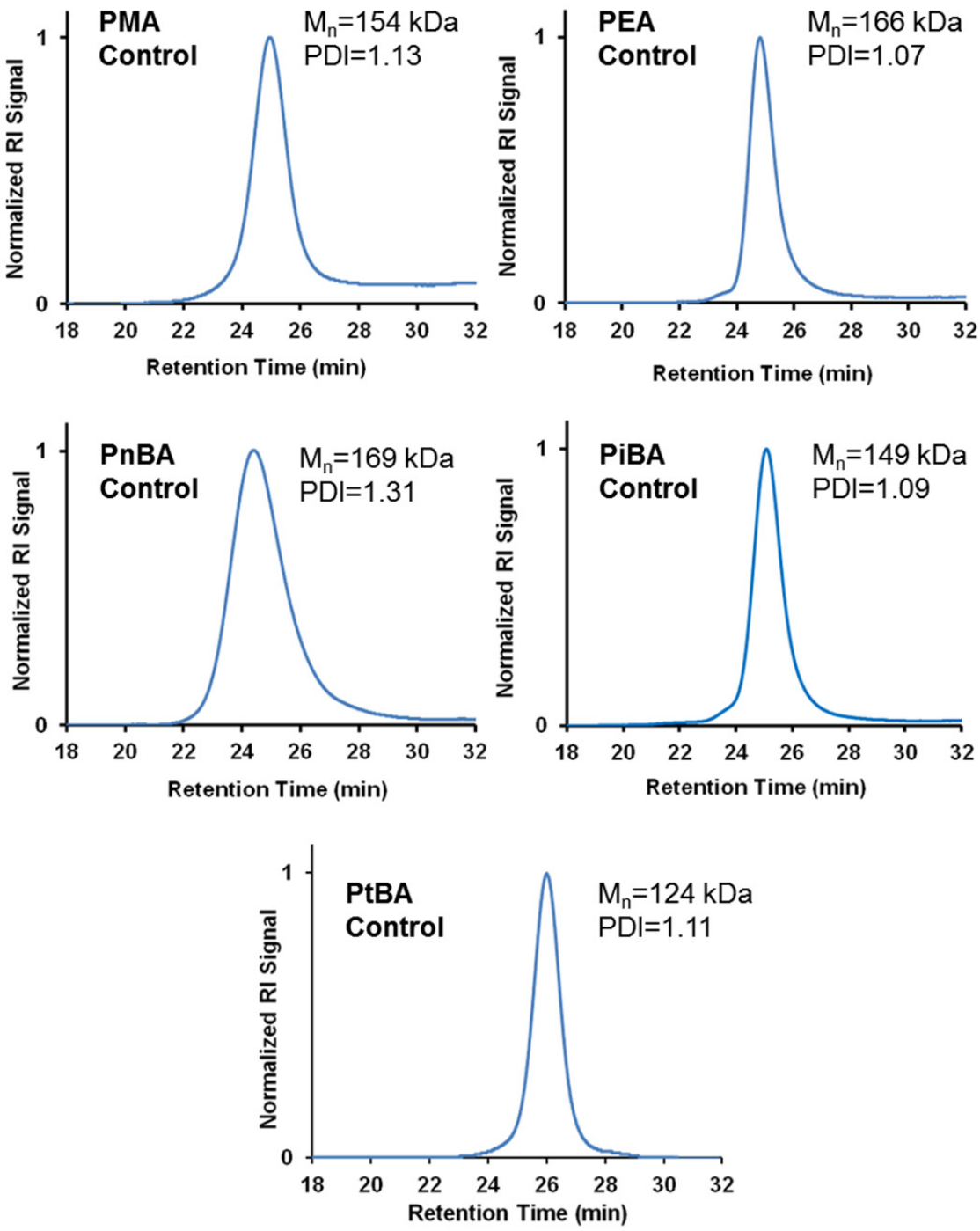


Figure S8. GPC traces of control polymers containing spiropyran at the chain-end.

VI. Sonication Procedures

General Method. A custom flow cell was constructed using a peristaltic pump to draw fluid from the reaction vessel (Suslick cell), flow it through a UV-Vis flow-through cuvette for light absorption measurements, and return the solution back to the reaction vessel continuously throughout the course of each experiment. Flow rates were held constant for each experiment unless otherwise specified. The total volume of the apparatus was 16 ml with 7.5 ml in the Suslick cell. The remaining 8.5 ml filled the Teflon tubing and cuvette. Additionally, the solutions were irradiated with continuous ultrasound at 20 kHz (10.7 W cm^{-2}). The Suslick cell was submerged in a cooling bath which was regulated by an immersion cooler to achieve a consistent internal temperature of 3–5 ºC of the reaction mixture in the Suslick cell throughout all experiments. Polymer solutions were continuously sonicated at a concentration of 1 mg mL^{-1} in methyl ethyl ketone (MEK) using argon as the saturation gas. The UV-Vis spectrometer was programmed to obtain either full spectra, absorbance at one wavelength or two wavelengths over time. Sonication intensity was calibrated according to the literature method.[3]

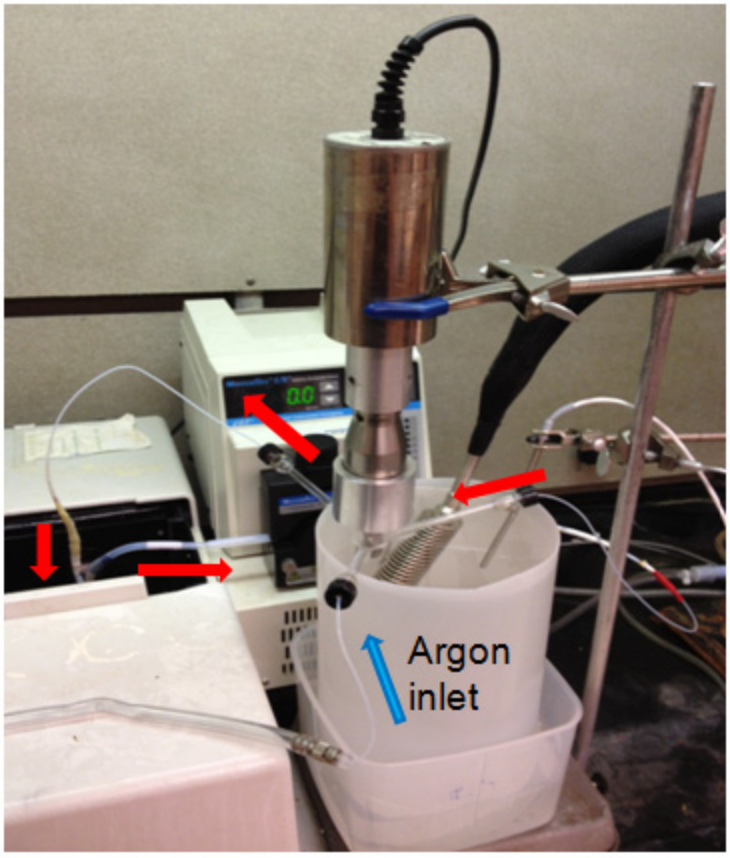


Figure S9. General set-up of the sonication flow cell apparatus. Liquid flow path is indicated by red arrows. Argon gas inlet is indicated with a blue arrow.

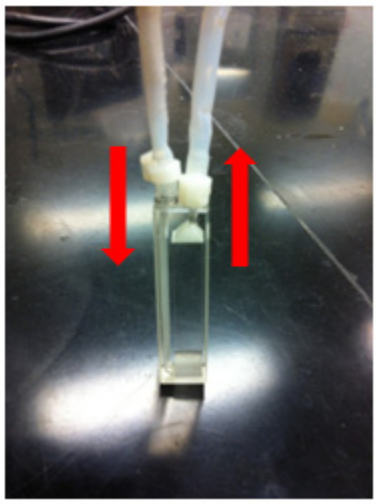


Figure S10. Image of the flow cell cuvette. Red arrows indicate the direction of flow.

General Procedure for Sonication Experiments. The sonication apparatus was assembled as shown in Figure S9 and S10. Polymer was dissolved at a concentration of 1 mg/ml in MEK and transferred to an oven-dried Suslick cell, which was placed into the collar and screwed onto the probe. An argon line, an inlet (to return solvent to the Suslick cell) and an outlet (to draw solvent from the Suslick cell) tube were each placed into the three arms of the Suslick cell, respectively. Argon was sparged through the system for 30 min prior to ultrasound irradiation and continued throughout the experiment. The Suslick cell was lowered into the acetone bath for 5 min prior to sonication. Longer cooling times resulted in the solution being so cold that water would condense on the cuvette. After 5 min of cooling, acquisition of UV-Vis absorption data was started followed immediately by ultrasound irradiation. The entire system was kept in the dark for the duration of the experiment.

Table S4: Temperature of acetone bath and corresponding solution temperature.

Instrument Amplitude (%)	Power Intensity (W cm^{-2})	Acetone Bath Temperature (°C)	Temperature of Solution in Suslick Cell (°C)
35%	10.7	-18 °C	3–5 °C

VII. Kinetic Analysis of Mechanophore Activation

Kinetics of spiropyran ring-opening were evaluated by the following equation[4]:

$$A_t = B(1 - e^{-kt}) \quad \text{(S2)}$$

where t equals sonication time, A_t equals the max absorbance of λ_{max} at time t, B is equal to the amplitude (maximum absorbance value), and k is the rate constant. Nonlinear least-squares fitting of the data with equation S2 gives the rate constant k. At any given time, 7.5 ml of

solution (out of the total 16 ml) was inside the Suslick cell being irradiated with ultrasound with the remaining 8.5 ml of solution outside of the Suslick cell not subjected to ultrasound. Therefore, actual "sonication time" was treated as 7.5/16 of real time. Drift in the obtained absorbance values were corrected by measuring the absorbance at 570 nm (λ_{max} of merocyanine) and 700 nm simultaneously during each experiment. The drift in absorbance values was unique to each experiment, therefore the absorbance at 700 nm was collected for every experiment and subtracted from the absorbance values at 570 nm for all calculations. Statistical analyses were performed as described in the literature.[5,6]

Table S5: Measured rate constants (min^{-1}, average of 2 runs) of mechanochemical activation for PMA, PEA, PnBA, PiBA, and PtBA in MEK at 3–5 °C, 1 mg/ml, and ultrasonication intensity of 10.7 W cm^{-2}.

PMA		**PEA**		**PnBA**		**PiBA**		**PtBA**	
$\mathbf{M_n}$	***k***	$\mathbf{M_n}$	***k***	$\mathbf{M_n}$	***k***	$\mathbf{M_n}$	***k***	$\mathbf{M_n}$	***k***
54	0.154	49	0.110	60	0.0594	60	0.0900	50	0.102
102	0.254	77	0.169	87	0.174	81	0.142	93	0.175
139	0.350	96	0.211	98	0.169	152	0.296	131	0.202
156	0.432	121	0.250	137	0.249	167	0.355	178	0.308
194	0.582	155	0.356	184	0.380	239	0.470	226	0.495
270	0.810	177	0.415	224	0.438	309	0.610	273	0.575
		233	0.569					292	0.610
		282	0.730						

VIII. References

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