

## SUPPORTING INFORMATION

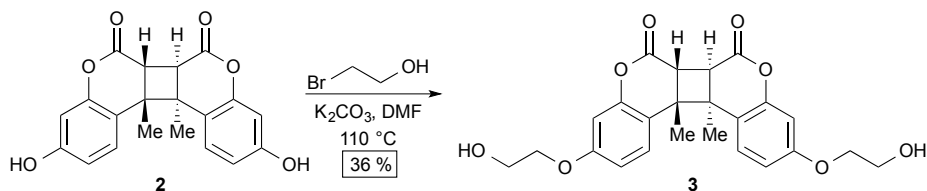
### **A Coumarin Dimer Probe of Mechanochemical Scission Efficiency in the Sonochemical Activation of Chain-Centered Mechanophore Polymers**

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#### **General Procedures**

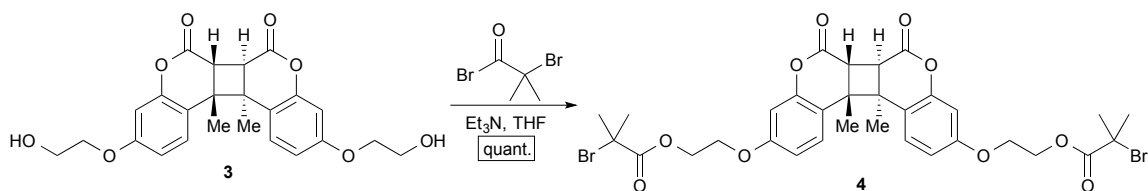
Coumarin dimer **2** was synthesized as previously described.<sup>1</sup> All other reagents were purchased from Sigma-Aldrich and used without further purification. CDCl<sub>3</sub> and DMSO-(d<sub>6</sub>) were purchased from Cambridge Isotope Laboratories. All other reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. Flash chromatography was performed on Silicycle F60 (230-400 mesh) silica gel. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to the residual solvent peak (CDCl<sub>3</sub> δ = 7.26 (<sup>1</sup>H) and 77.16(<sup>13</sup>C), DMSO-(d<sub>6</sub>) δ = 2.50 (<sup>1</sup>H) and 39.52 (<sup>13</sup>C)) were collected on either a Varian INOVA 400 MHz or 500 MHz spectrometer as noted. Gel permeation chromatography was performed on two in series columns (Agilent Technology PL gel 10<sup>4</sup> Å, 10<sup>3</sup> Å) with THF as the mobile phase at 0.5 mL min<sup>-1</sup> with the flow rate set with a Varian Prostar Model 210 pump. Molecular weights were determined using an in-line Wyatt Dawn EOS multi-angle light scattering (MALS) detector and a Wyatt Optilab DSP Interferometric Refractometer (RI). The dn/dc values were determined at room temperature in THF using in-line RI detection.

#### **Synthesis**



**2** (1.05 g, 2.98 mmol) and  $K_2CO_3$  (1.64 g, 11.9 mmol) were suspended in anhydrous DMF (20 mL) in an oven dried 100 mL round bottom flask with stirring. 2-Bromoethanol (0.64 mL, 9.0 mmol) was then added and the suspension heated at 110 °C under argon overnight. The mixture was then allowed to cool to room temperature and poured into 100 mL HCl (10 %, aq.) and extracted with EtOAc (3 x 100 mL), dried over  $MgSO_4$ , and evaporated under reduced pressure. The solid residue was then taken up into hot EtOAc and filtered to remove any unreacted starting material. The filtrate was evaporated under reduced pressure to yield **3** as a white solid (475 mg, 36 %).

$^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  (ppm): 7.33 (2H, d,  $J = 8.6$ ), 6.84 (2H, d,  $J = 8.6$ ), 6.70 (2H, s), 4.88 (2H, t,  $J = 5.6$ ), 4.02 (4H, t,  $J = 4.0$ ), 3.72 (4H, m), 3.44 (2H, d,  $J = 1.8$ ), 1.13 (6H, s);  $^{13}C$  NMR (125 MHz,  $DMSO-(d_6)$ )  $\delta$  (ppm): 165.79, 159.00, 151.05, 129.19, 115.28, 111.80, 102.41, 69.93, 59.46, 45.91, 43.86, 26.27; HRMS-ESI:  $m/z =$  Found 441.1547 ( $[M+H]^+$ ); calc. 441.1544.



**3** (471 mg, 1.07 mmol) was suspended in THF (15 mL) in a flame dried 50 mL round bottom flask. Anhydrous  $Et_3N$  (0.74 mL, 5.4 mmol) was then added by syringe, followed by  $\alpha$ -bromoisobutyryl bromide (0.40 mL, 3.2 mmol) dropwise and allowed to stir for 72 hr under argon. The solution was then filtered and evaporated under reduced pressure. The yellow residue was then purified by column chromatography ( $SiO_2$ , gradient  $CH_2Cl_2$  to 98:2  $CH_2Cl_2$ :MeOH) to yield **4** as a crystalline solid in quantitative yield (793 mg, 1.07 mmol).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.05 (2H, d,  $J = 8.6$ ), 6.79 (2H, dd,  $J = 2.6, 8.6$ ), 6.64 (2H, d,  $J = 2.6$ ), 4.53 (4H, m), 4.23 (4H, m), 3.36 (2H, s), 1.94 (12H, s), 1.23 (6H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 171.70, 165.95, 159.24, 151.74, 128.30, 115.76, 112.51, 103.51, 66.04, 64.00, 55.54, 46.75, 45.08, 30.82, 26.50; HRMS-ESI:  $m/z = \text{Found } 737.0591$  ( $[\text{M}+\text{H}]^+$ ); calc. 737.0591.

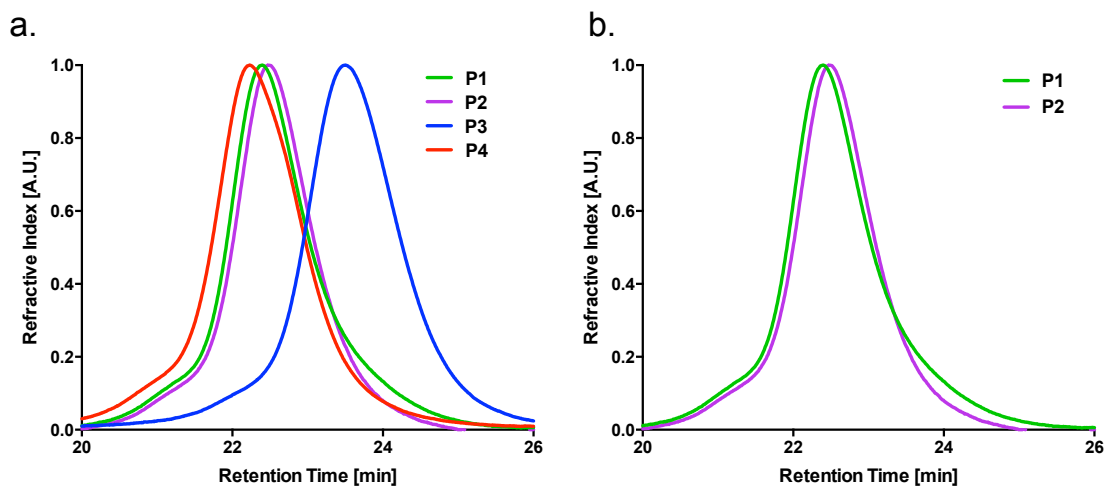
## Polymer Preparation

### Synthesis

All polymers were initially synthesized by the following method: An oven dried Schlenk flask with side arm and septum was charged with a copper wire (2 cm) wrapped stirbar, di-initiator **4** (1 equiv.), methyl acrylate (1400 equiv.), and DMSO (2:1 v/v DMSO: methyl acrylate). The solution was subjected to 3 freeze-pump-thaw cycles before backfilling with argon and placing in a thermostated bath at 25 °C.  $\text{Me}_6\text{TREN}$  (2 equiv.) was added by syringe to initiate the polymerization. The reaction was terminated upon exposure to air, and was subsequently diluted with a minimal amount of  $\text{CH}_2\text{Cl}_2$ , and was precipitated into cold MeOH. Precipitation was repeated twice more from  $\text{CH}_2\text{Cl}_2$  into cold MeOH. Drying by high vacuum yielded a gummy-translucent polymer.

### Fractionation

Polymers P2-P4 were subjected to fractionation by preparatory GPC before sonication. (Polymer fractionation was performed via preparatory GPC chromatography on two in series columns (Waters Ultrastyrigel 19x300 mm columns,  $10^4\text{\AA}$  and  $10^5\text{\AA}$ ) with THF as the mobile phase. The flow rate was set to 1 ml/min with a Varian ProStar Model 210 pump. The polymer distribution was observed by refractive index (Waters 2414 Refractive Index Detector) and fractions were collected near the peak maximum in order to narrow the molecular weight distribution.



**Figure S 1.** (a) GPC-RI traces of the polymers described in Table 1 of the main text. (b) GPC-RI for P1 and P2 showing the effect of fractionation.

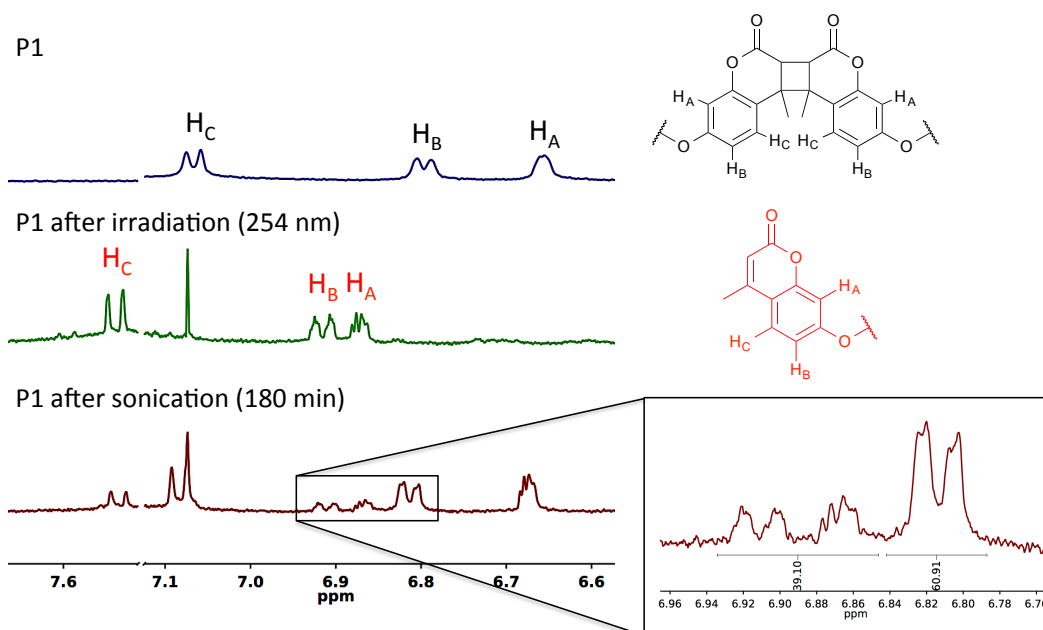
## General Sonication Conditions

Ultrasound experiments were performed in dry acetonitrile on a Vibracell Model VCX500 (20 kHz frequency) with a 12.8 mm titanium probe. For polymer **4**,  $\text{CHCl}_3$  was used due to insolubility in acetonitrile while all other conditions were identical. Solutions were irradiated at a concentration of 2 mg/mL in 16 mL of solvent unless otherwise noted. Prior to sonication, the solution was transferred to a 3-necked Suslick cell in an ice bath and sparged with nitrogen for 30 minutes prior to sonication. Irradiations were performed at  $14.8 \text{ W/cm}^2$  with a pulse sequence of 1s on/1s off while maintaining a temperature of 6–9 °C under a nitrogen atmosphere. Power calibration was performed using the method of Berkowski et. al.<sup>2</sup>

Individual sonication experiments were performed for each time point. 32 mg of **P1** was dissolved in 16 mL MeCN, subjected to irradiation for the times indicated. The solution was filtered and evaporated under reduced pressure. A 2 mg sample was dissolved in 1 mL of THF for GPC analysis, while the remainder was dissolved in 0.5 mL  $\text{CDCl}_3$  for NMR analysis.

## Modeling

Inverse transform sampling method was used to generate a representative population ( $N = 10,000$ ) of coumarin chain-end polymers based on cumulative probability distribution data obtained from GPC-MALS derived number averaged MW distributions of photolyzed polymers (**P1-4 UV**). Chains were then randomly paired to create a population of chains ( $N = 5000$ ) with known molecular weight and mechanophore location, a reasonable simulation of the same distributions in the original polymers (**P1-4**) assuming that the chains on either side of the mechanophore grow independently of each other during polymer synthesis.

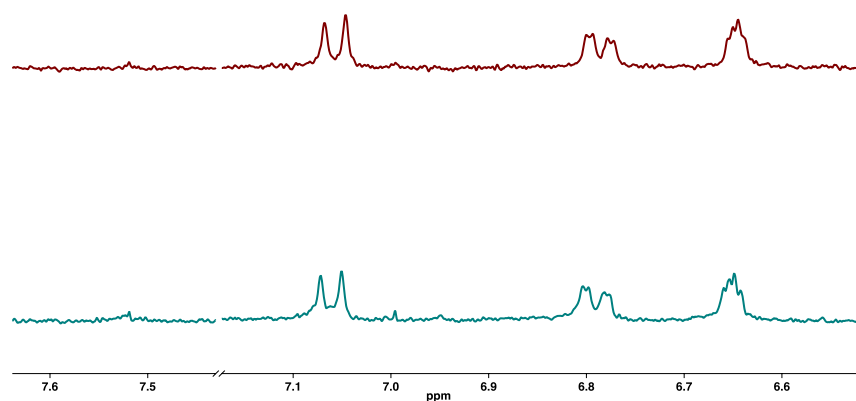


**Figure S 2.** Truncated  $^1\text{H}$  NMR spectra showing chain-centered CD and chain-end coumarin peaks for P1 (blue), P1 after irradiation @ 254 nm (green), and P1 after sonication (red).

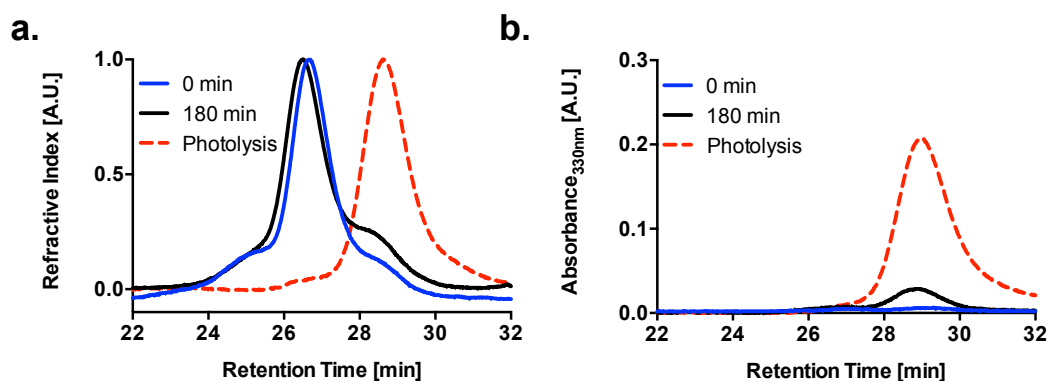
### Sonication of Control Polymer

A low molecular weight ( $M_n = 28$ , PDI = 1.04) control polymer was synthesized in a manner identical to P1-P4 and subjected to identical sonication and photolysis conditions. After 180 min of sonication, no

discernible free coumarin was observed by  $^1\text{H}$  NMR, while minimal molecular weight degradation and increased UV absorbance was observed by GPC. This lack of reactivity towards ultrasound relative to the high MW counterparts indicates that the CD unit reacts mechanochemically rather than due to purely thermal or radical induced processes.

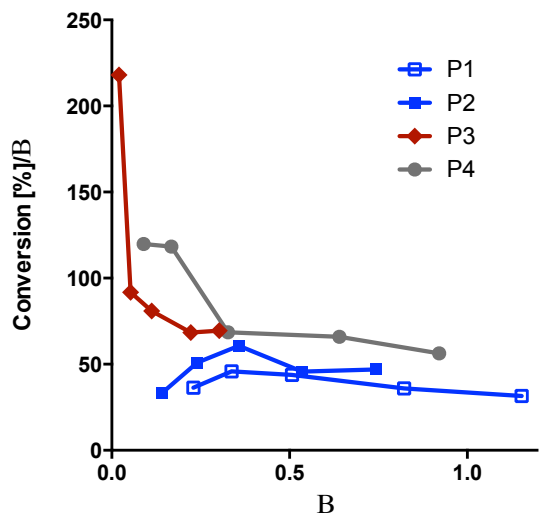


**Figure S 3.**  $^1\text{H}$  NMR spectrum showing region containing peaks diagnostic of CD and free coumarin for control polymer (28 kDa) before (top) and after (bottom) sonication for 180 min.



**Figure S 4.** GPC traces of 28 kDa polymer (dark blue), the same polymer after sonication (180 min, black), and after photolysis (red, dashed). (a) RI detection showing minimal molecular weight degradation by

sonication relative to that from photolysis. (b) UV detection ( $\lambda_{\text{detection}} = 330 \text{ nm}$ ) showing low efficiency of coumarin generation relative to photolyzed control. Scission and activation are both very low compared to Figure 1 in the main text.



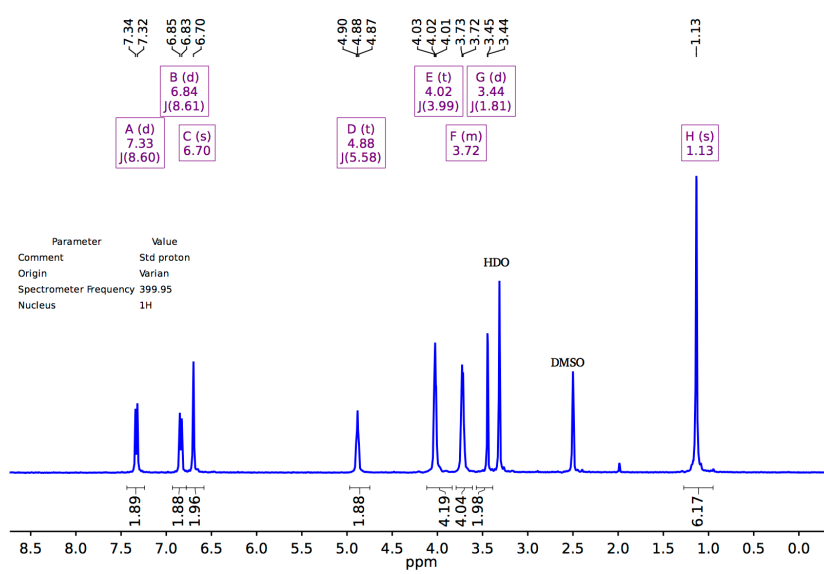
**Figure S 5.** Conversion per break vs. number of breaks for polymers P1-4. The relative order in efficiencies of activation for polymers P1-4 does not change as a function of average breaks per chain (B). Note that data at low levels of breaking ( $B < 0.25$ ) intrinsically contain high uncertainty.

## References

1. Suzuki, H. & Tamura, T. PROCESS FOR PRODUCTION OF COUMARIN DIMER COMPOUND. US 8,258,318 B2 (2012).
2. Berkowski, K. L., Potisek, S. L., Hickenboth, C. R. & Moore, J. S. Ultrasound-induced site-specific cleavage of azo-functionalized poly(ethylene glycol). *Macromolecules* (2005) **38**, 8975-8978.

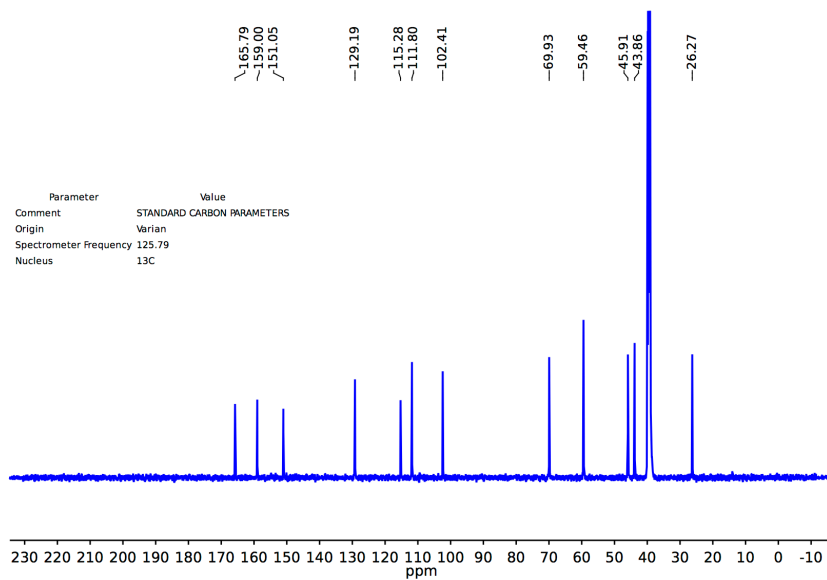
# NMR Spectra

## <sup>1</sup>H NMR Spectrum of **3**

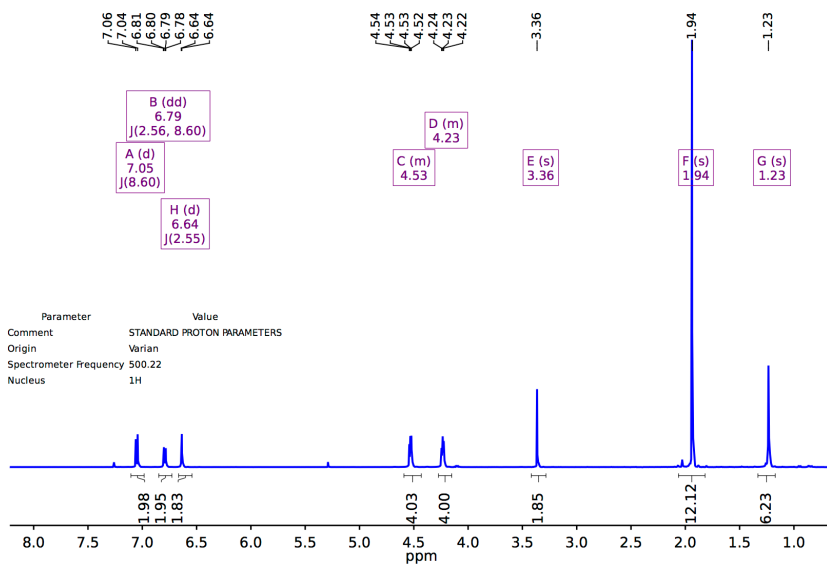


## <sup>13</sup>C NMR Spectrum of **3**





### <sup>1</sup>H NMR Spectrum of 4



### <sup>13</sup>C NMR Spectrum of 4

171.70  
165.95  
159.24  
151.74  
-128.30  
-115.76  
-112.51  
-103.51  
66.04  
64.00  
32.54  
17.02  
45.08  
-30.82  
-26.50

Parameter Value  
Comment STANDARD CARBON PARAMETERS  
Origin Varian  
Spectrometer Frequency 125.79  
Nucleus 13C

