## Supporting Information for

## Force-Induced Cleavage of a Labile Bond for Enhanced Mechanochemical Crosslinking

Melissa B. Gordon<sup>a,b</sup>, Shu Wang<sup>b</sup>, Grant A. Knappe<sup>b</sup>, Norman J. Wagner<sup>b</sup>, Thomas H. Epps, III<sup>b,c</sup>, Christopher J. Kloxin<sup>b,c\*</sup>

<sup>a</sup>Department of Chemical and Biomolecular Engineering, Lafayette College, Easton, PA, 18042, USA

<sup>b</sup>Department of Chemical and Biomolecular Engineering, Center for Molecular and Engineering Thermodynamics, University of Delaware, Newark, DE 19716, USA

<sup>c</sup>Department of Material Science and Engineering, University of Delaware, Newark, DE 19716, USA

Polymer Synthesis: Dibenzyl trithiocarbonate (CAS: 26504-29-0) was purchased from Sigma Aldrich and used as received. n-Butyl acrylate (CAS: 141-32-2) also was purchased from Sigma Aldrich and passed through a basic alumina column to remove the inhibitor before use. 2,2'-Azobisisobutyronitrile (AIBN, CAS: 78-67-1) was purchased from Sigma Aldrich and recrystallized twice from methanol before use. AIBN, *n*-butyl acrylate, and dibenzyl trithiocarbonate were dissolved in an anisole solution containing 5 wt% dimethylformamide (DMF) at the concentrations given in Table S1. The mixture was transferred into a Schlenk tube equipped with a stir bar and stopcock, after which, the mixture was degassed by three freeze-thawpump cycles. The Schlenk tube was backfilled with argon (3-4 psig), sealed, and heated in an oil bath at 72 °C for the time indicated in Table S1. The reaction mixture was diluted with tetrahydrofuran (THF) (2-fold dilution) and precipitated in a methanol/water (60/40, v/v) mixture (10-fold dilution). The upper layer of solution was decanted, and the polymer (pale yellow viscous liquid) was collected and dried under vacuum for 2 days. The molecular weight of the polymers was determined by gel permeation chromatography (GPC) in THF using polystyrene standards. The poly(*n*-butyl acrylate) (PBA) (162 kDa and 124 kDa) without the trithiocarbonate (TTC) mechanophore (i.e., control samples) were purchased from Polymer Source and used as received.

transfer (RAI	FT) polymerization	s with corresp	ponding po	olymer pro	perties. (N	1: monome	er, CTA:	
chain transfer	r agent, S: solvent;	$M_{n,calc}$ : molec	cular weigl	nt calculate	ed based o	n conversi	on	
(determined)	by <sup>1</sup> H NMR), <i>Đ</i> : di	spersity)						
Polymer	[M] <sub>0</sub> /[CTA] <sub>0</sub> /	[S]/[M] <sub>0</sub>	Time	Conv	M <sub>n,calc</sub>	M <sub>n,GPC</sub>	M <sub>w,GPC</sub>	Ð
	[AIBN] <sub>0</sub>	(wt/wt)	( <b>h</b> )		(kDa)	(kDa)	(kDa)	
	(mol/mol/mol)							
54 kDa	506/1/0.12	0.5/1	5	95%	62.0	54.1	62.0	1.15

8

79%

168.2

130.0

165.7

1.27

<b>Table S1</b> : Concentrations and reaction conditions for reversible addition fragmentation chain
transfer (RAFT) polymerizations with corresponding polymer properties. (M: monomer, CTA:
chain transfer agent, S: solvent; $M_{n,calc}$ : molecular weight calculated based on conversion
(determined by <sup>1</sup> H NMR), <i>D</i> : dispersity)

Radical Trap Experiments: Solutions (10 g) containing a 2,2,6,6-tetramethyl-1piperidinyloxy (TEMPO) radical trap (Sigma Aldrich, CAS: 2564-83-2, 0.1 wt%) and the TTC-

1/1

130 kDa

1658/1/0.10

containing polymer (0.5 wt%) were prepared using butylated hydroxytoluene (BHT)-free THF (Fisher, CAS: 109-99-9). The solutions were kept in an ice bath and sonicated under continuous nitrogen flow (0.05 SCFH) using a 13 mm diameter probe and Model W-225R sonicator from Heating Systems Ultrasonics, Inc (200 W, 20% amplitude, 20 kHz).

*Gelation Experiments:* All solutions (10 g) were prepared using BHT-free THF (Fisher, CAS: 109-99-9). The tetraethylene glycol diacrylate (TEGDA, TCI America, CAS: 17831-71-9) was passed through a basic alumina plug to remove inhibitor before use. For the thiol-ene polymerization, pentaerythritol tetra (3-mercaptopropionate) (PETMP, Evan's Chemetics, CAS: 7575-23-7, 18 wt%) and triethylene glycol divinyl ether (TEGDVE, Sigma Aldrich, CAS: 765-12-8, 15 wt%) were used as received. The solutions were kept in an ice bath and continuously sonicated until gelation using the same sonicator and probe as described above. Nitrogen was bubbled through the solution for the duration of the experiment (1 SCFH).

*Light Experiments:* Solutions were prepared as described above and irradiated with  $26 \text{ mW/cm}^2$  of 365 nm light for 4 h.

Secondary Control in Radical Trap Experiments: Figure 2 contains a comparison of a TTC-containing polymer of  $M_n = 130$  kDa to a control polymer of similar molecular weight ( $M_n = 124$  kDa). Recognizing that polymer cleavage is a function of molecular weight and that there is a small (6 kDa) discrepancy in molecular weight between the TTCcontaining polymer and control shown in Figure 2, a solution containing a second PBA control polymer (i.e., not possessing the central TTC moiety) of higher molecular weight ( $M_n = 162$  kDa) was subjected to the same sonication conditions as the polymers shown in Figure 2 to further assess the effect of the central TTC moiety on chain cleavage. As shown in Figure S1, this secondary control polymer also showed reduced cleavage during sonication compared to TTC- containing polymer (Figure 2) further verifying the enhanced chain scission imparted by the TTC moiety in response to sonication.



**Figure S1:** Time evolution of the cleavage during sonication of the secondary PBA control polymer of higher molecular weight ( $M_n$ =162 kDa).

*Replicate Sonication Experiment:* Figures 3A and 3B show representative plots of the time evolution of the TTC-containing polymer and the PBA control in response to sonication. This result is reproducible as shown in Figure S2.



**Figure S2:** Time evolution of the cleavage during sonication of the TTC-containing polymer (130 kDa) and the PBA control. All conditions were identical to that described in Figure 3.

*Intermediate Molecular Weight Study:* The response of a TTC-containing polymer of intermediate molecular weight (107 kDa) and its control (101 kDa) to sonication is shown in Figure S3. We note that the polymer containing the labile TTC moiety shows an enhanced cleavage following sonication compared with the control (i.e., not containing central TTC moiety).



**Figure S3:** The GPC trace of the mechanophore-containing polymer (107 kDa) exhibited enhanced force-induced cleavage following 30 min of sonication (A) compared to a control polymer of similar molecular weight (101 kDa) that did not contain the central TTC moiety (B).

*Gelation via Thiol-ene Polymerization:* As discussed above, the stress-responsive polymer ( $M_n = 130 \text{ kDa}, 0.5 \text{ wt\%}$ ) was dissolved in THF (10 mL) with divinyl ether (triethylene glycol divinyl ether, TEGDVE, 15 wt%) and tetra-thiol (pentaerythritol tetra (3-mercaptopropionate), PETMP, 18 wt%) monomers. Sonication of the solution resulted in gelation via a thiol-ene polymerization, as shown below.

 Before Sonication (liquid)
 After Sonication (gel)

 Image: After Sonication (gel)
 Image: After Sonication (gel)

 Image: After Sonication (gel)
 Image: After Sonication (gel)

**Figure S4:** Gelation via a thiol-ene polymerization resulted following sonication. The vial was inverted to indicate the formation of the gel after sonicating the liquid solution.

*NMR Spectroscopy Experiments:* We conducted carbon NMR measurements to investigate the TTC bond in response to sonication and light. Solutions containing TEMPO and the TTC-containing polymer were prepared as described above and subjected to the aforementioned sonication and irradiation conditions. In this experiment, the solutions were pulsed for 15 minutes and then continuously sonicated for an additional 15 minutes. The solvent was evaporated and the product was dissolved in deuterated chloroform for NMR. As shown in Figure S5, in response to sonication, the 174.5 ppm peak corresponding to the carbon in the TTC moiety of the polymer remains and two additional peaks at 161.3 ppm and 178.1 ppm appear. We note the emergence the same two peaks following UV irradiation of the TTC-containing polymer. As UV light is known to cleave the labile carbon-sulfur bond of the TTC moiety, these results also

suggest cleavage of the polymer chain at the central TTC moiety during sonication and are consistent with the results in the Figure 2B and 2C of the main text.

## **Response to Sonication**



**Figure S5:** Comparison of the carbon NMR spectra of the TTC-containing polymer following exposure to sonication and light suggests cleavage of the polymer chain at the TTC moiety.