**Supporting Information**

**Enhanced Polymer Mechanical Degradation through Mechanochemically Unveiled Lactonization**

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# **General procedures**

## **Materials**

Lab general solvents (hexane, ethyl acetate, dichloromethane, toluene, tetrahydrofuran, acetonitrile, methanol) were purchased from VWR or Sigma Aldrich. Tetrahydrophthalic anhydride (THPA), 2-butyne-1,4-diol, 3-buten-1-ol, benzophenone, *p*-toluenesulfonic acid (pTSA), 3,4-Dihydro-2*H*-pyran, 9-oxabicyclo[6.1.0]non-4-ene and Grubbs II catalyst were purchased from Sigma Aldrich, Alfa Aesar, Acros or TCI and used without further purification.

## **Characterizations**

1H NMR spectra were collected on a Bruker Advance Neo-500 MHz multinuclear NMR spectrometer. Chemical shifts are provided in *ppm* (δ) and referenced to the residual 1H peak at 7.26 ppm in CDCl3. 1H shifts are reported as chemical shift, multiplicity, coupling constant if applicable, and relative integral. Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt), triplet (t), triplet of doublets (td), quartet (q), pentet (p), multiplet (m), or broad (br). Coupling constants (J) are reported in Hertz. High-resolution mass spectra were collected on an Agilent LCMS-TOF-DART at Duke University’s Mass Spectrometry Facility.

Photoreaction was conducted using a photochemical reactor from The Southern New England Ultraviolet Company (Model #RPR-100, RPR2537A/254 nm bulb).

Ultrasonication was performed with a Sonics VCX 750 generator using a 13 mm tip. Pulsed ultrasound (1s on, 1s off) was applied under N2 atmosphere while cooled with an ice bath. Aliquot was taken from the solution and subjected to GPC and 1H NMR analysis.

Gel permeation chromatography (GPC) was performed on two Agilent PLgel mixed-C columns (105 Å, 7.5x300 mm, 5 μm, part number PL1110-6500) using THF (stabilized with 100 ppm BHT) as the eluent. Molecular weights were calculated using a Wyatt Dawn EOS multi-angle light scattering (MALS) detector and Wyatt Optilab DSP Interferometric Refractometer (RI). The refractive index increment (dn/dc) values were determined by online calculation based on injections of known concentration and mass.

Sharp Microlever silicon probes (MSNL) and Silicon Nitride AFM Probes (PNP-DB) were correspondingly purchased from Bruker (Camarillo, CA) and NanoAndMore(Watsonville, CA). All of the SMFS studies were conducted at ambient temperature (~23 °C) using a homemade AFM, which was constructed using a Digital Instruments scanning head mounted on top of a piezoelectric positioner, similar to the one described in detail previously.1-2 The AFM pulling experiments were conducted in a solution of toluene. The spring constant of each cantilever was calibrated in air, using the thermal noise method, based on the energy equipartition theorem as described previously.1-2 Measurements were carried out in a closed fluid cell with a scanning set for a series of approaching/retracting cycles. Probes were prepared by immersing in piranha solution (H2SO4: H2O2 = 3:1) for 15 minutes at room temperature and then immersing in deionized water and dried by touching them against a borohydride. Silicon substrates were prepared by first allowing each to soak in hot piranha solution for 30 minutes and then washed with deionized water and dried under a stream of nitrogen. Caution should be used when handling piranha solution: it has been reported to detonate unexpectedly. The substrate and the cantilever were then placed in a UVO cleaner (ozone produced through UV light) for 15 minutes. After ozonolysis, the cantilever was mounted in the fluid cell. 20 μL of a 0.05-0.1 mg/mL polymer solution was added to the silicon substrate surface and allowed to dry. The silicon substrate was then placed on the piezoelectric stage of the AFM. Force curves were collected in dSPACE (dSPACE Inc. Wixom, MI) and analyzed using Matlab (The MathWorks, Inc., Natick, MA). All data were filtered during acquisition at 500 Hz. After acquisition, the data were calibrated and plotted by using homemade software written in Matlab language.

# **Synthesis details**

## **Synthesis scheme**



## **Synthesis of small molecules**

### Synthesis of compound **1**



The synthesis of compound **1** was performed using adapted procedures according to previous literature.3-6

To a 500 mL quartz flask, added tetrahydrophthalic anhydride (THPA) (2.28 g, 15 mmol), 2-butyne-1,4-diol (1.835 g, 22.5 mmol) and benzophenone (900 mg). 188 mL CH3CN was then added to dissolve the compounds and the solution was sparged with N2 for 10 min. The flask was capped and irradiated with UV 254 nm light for 6 h. The resulting pale-orange solution was condensed. Product was purified by chromatography using 0~70% EtOAc/hexane gradient eluent. Compound **1** was isolated as a pale-yellow solid (2.536 g, 1H NMR indicates 1:1 molar ratio of product **1** to 2-butyne-1,4-diol, 52.2% yield). 1H NMR (500 MHz, CDCl3) δ: 4.31 (s, 4H), 2.14 – 1.91 (m, 4H), 1.72 – 1.59 (m, 2H), 1.59 – 1.45 (m, 2H). 13C NMR (125 MHz, CDCl3) 13C NMR (125 MHz, CDCl3) δ: 171.77, 145.08, 57.73, 51.27, 24.21, 19.45. HRMS-ESI (*m/z*): [M+H]+ calculated for C12H15O5, 239.09140; observed, 239.09204.

### Synthesis of compound **2**



To a 50 mL round bottom flask, added compound **1** (1.19 g, 3.67 mmol compound **1**), *p*TSA (47 mg, 0.25 mmol) and 20 mL 3-buten-1-ol. The solution was then heated at 80 oC for 2d. The excess 3-buten-1-ol was then distilled under reduced pressure. Resulting yellow viscous mixture was purified by chromatography (0~50% EtOAc/hexane) to give compound **2** as a pale-yellow oil (659 mg, 49.3%). 1H NMR (500 MHz, CDCl3) δ: 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 5.18 – 5.03 (m, 4H), 4.32 – 4.17 (m, 4H), 4.08 (t, *J* = 6.7 Hz, 4H), 2.36 (qt, *J* = 6.7, 1.4 Hz, 4H), 2.21 – 2.06 (m, 2H), 1.87 – 1.76 (m, 2H), 1.69 – 1.59 (m, 2H), 1.56 – 1.44 (m, 2H). 13C NMR (125 MHz, CDCl3) δ: 173.75, 143.13, 134.08, 117.57, 64.14, 58.06, 55.98, 33.09, 25.18, 16.10. HRMS-ESI (*m/z*): [M+H]+ calculated for C20H29O6, 365.19587; observed, 365.19625.

### Synthesis of compound **3**



To a solution of compound **2** (364 mg, 1 mmol) in 10 mL DCM, added 3,4-dihydropyran (364 mg, 4 mmol) and *p*TSA (17 mg, 0.1 mmol). The solution was stirred at room temperature for 2 h. DCM was then removed and resulting oil was subjected to chromatography (0~30% EtOAC/hexane) to give compound **3** as a clear oil (322 mg, 60.5%). 1H NMR (500 MHz, CDCl3) δ: 5.77 (ddt, *J* = 17.0, 10.2, 6.9Hz, 2H), 5.15 – 5.00 (m, 4H), 4.64 (t, *J* = 3.3 Hz, 2H), 4.53 – 4.45 (m, 1H), 4.36 (dd, *J* = 13.2, 9.0 Hz, 1H), 4.26 – 4.18 (m, 1H), 4.16 – 4.11 (m, 1H), 4.11 – 3.99 (m, 4H), 3.87 – 3.74 (m, 2H), 3.55 – 3.46 (m, 2H), 2.35 (dddd, *J* = 9.0, 7.7, 4.7, 1.6 Hz, 2H), 2.18 – 2.07 (m, 2H), 1.93 – 1.83 (m, 2H), 1.83 – 1.72 (m, 2H), 1.72 – 1.45 (m, 14H).. 13C NMR (125 MHz, CDCl3) δ: 173.52, 141.58, 141.51, 134.25, 134.22, 117.30, 117.27, 98.13, 98.02, 63.80, 63.78, 63.75, 62.51, 62.47, 62.28, 62.26, 61.66, 61.62, 61.53, 61.51, 56.04, 56.01, 55.94, 33.17, 33.15, 31.74, 30.55, 30.53, 30.52, 26.13, 26.00, 25.92, 25.74, 25.63, 22.80, 19.10, 19.09, 19.07, 19.04, 16.13, 16.11, 16.08, 16.05, 14.27. HRMS-ESI (*m/z*): [M+Na]+ calculated for C30H44O8Na, 555.29284; observed, 555.29235.

### Synthesis of compound **4**



A solution of compound **3** (112 mg, 0.23 mmol) in 115 mL DCM was sparged with N2 for 10 min, Grubbs II catalyst (20 mg, 0.023 mmol) was then added in one portion. The solution was heated at 41 oC for overnight. After the reaction completed, 0.2 mL of ethyl vinyl ether was added to quench the reaction and the solution was further stirred for 30 min. Resulting solution was rotavaped onto silica and purified by chromatography (0~30% EtOAc/hexane) to give compound **4** as an off-white solid (107 mg, 93%). Compound **4** was further recrystallized from hexane. 1H NMR (500 MHz, CDCl3) δ: 5.55 – 5.37 (m, 2H), 4.71 – 4.58 (m, 2H), 4.52 – 3.94 (m, 6H), 3.87 – 3.74 (m, 2H), 3.57 – 3.44 (m, 2H), 2.50 – 2.31 (m, 2H), 2.31 – 2.20 (m, 2H), 2.19 – 2.06 (m, 2H), 1.91 – 1.82 (m, 2H), 1.82 – 1.73 (m, 2H), 1.73 – 1.43 (m, 12H). 13C NMR (125 MHz, CDCl3) δ: 173.67, 173.52, 141.56, 141.22, 129.11, 129.08, 129.06, 128.61, 98.01, 97.95, 97.85, 63.42, 63.37, 63.31, 62.49, 62.23, 62.18, 61.65, 61.61, 61.31, 56.26, 56.22, 56.19, 31.15, 31.11, 31.08, 31.06, 30.52, 30.50, 27.54, 26.51, 26.28, 26.07, 25.78, 25.64, 19.09, 18.96, 18.93, 16.09, 16.05. HRMS-ESI (*m/z*): [M+NH4]+ calculated for C28H44NO8, 522.30614; observed, 522.30747.

## **Synthesis of polymers**

### Synthesis of polymer **P1**



Monomer **4** (15.1 mg, 0.03 mmol) and 9-oxabicyclo[6.1.0]non-4-ene (epoxy-COD, 8.7 mg, 0.07 mmol) was weighted in a 10 mL frame-dried scintillation vial and kept under N2. 0.1 mL of N2 sparged Grubbs II catalyst solution (1.4 mg in 2 mL toluene) was added to the monomers. The polymerization was performed overnight, after which several drops of ethyl vinyl ether were added. The viscous solution was further stirred for 30min. After two rounds of precipitation from methanol, the resulting white polymer was dissolved in 1 mL DCM under stirring, and MeOH was added dropwise into the solution until it turned cloudy. The vial was capped and subjected to centrifuge at 4500 rpm for 10 min. The Upper clear solution was decanted and the polymer layer at the bottom was washed with MeOH and dried under high vacuum. This high molecular weight portion polymer was further used for SMFS study.

### Synthesis of polymer **P2**



To a 10 mL frame-dried scintillation vial, added monomer **4** (25 mg, 0.05 mmol) and 9,9-dichlorobicyclo[6.1.0]non-4-ene7-9 (gDCC-COD, 38.2 mg, 0.2 mmol). The vial was purged and kept under N2. 0.25 mL of N2 sparged Grubbs II catalyst solution (1.6 mg in 2 mL DCM) was added. After the polymerization was stirred for overnight, several drops of ethyl vinyl ether were added, and the solution was further stirred for 30 min to quench the catalyst. After three rounds of precipitation from methanol, a white polymer was obtained (52 mg, 82%). 1H NMR spectra indicated 14 mol% incorporation of monomer **4**. GPC-MALS: Mn = 128.4 kDa. PDI = 1.39, dn/dc = 0.114.

### Synthesis of polymer **P3**



To a solution of 25 mg **P2** polymer in 1.5 mL DCM/MeOH (2:1), added 1 mg pTSA catalyst. After stirred for overnight, the solution was condensed and precipitated from MeOH. Obtained white polymer was dried under high vacuum (20 mg, ). 1H NMR indicated selective removal of THP protecting group. The polymer was analyzed from GPC-MALS: Mn = 119.8 kDa. PDI = 1.62, dn/dc = 0.124.

# **Sonication experiment**

## **General sonication procedures**

A solution of polymer **P2** (1.2 mg/mL) and **P3** (1.0 mg/mL) in dry THF was transferred into a dry Suslick cell. The solution was sparged with N2 for 10 min while cooled with ice bath. Pulsed ultrasound was applied (1s on, 1s off) at 30% amplitude. Aliquots of 0.8 mL sample at various sonication times (0, 5, 10, 20, 30, 45, 60 min) were took from the cell and analyzed by GPC. After GPC analysis, each remained samples was transferred into a 10 ml scintillation vial and condensed. Resulting polymer was further dried under high vacuum and then subjected to 1H NMR analysis to quantify the amount of ring opened BCOE and *g*DCC mechanophores.

## **Analysis of mechanical activation**

### Ultrasonication of **P2** polymer

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**Figure S1.** GPC traces of **P2** polymer (left) and corresponding Mn evolution (right) at various sonication time.

The number of chain scission cycle (SC) was calculated according to the following equation:

is the initial molecular weight and is the sonicated molecular weight.



**Figure S2.** Scission cycles of **P2** polymer at various sonication times.

The activation of *g*DCC and BCOE mechanophores were analyzed from 1H NMR spectrum. The ring-opening (RO) percentage of *g*DCC and BCOE are calculated from the following equations:

;

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**Figure S3.** Stack of 1H-NMR (CDCl3, 500 MHz) spectra of sonicated **P2** polymer at various sonication time.



**Figure S4.** Ring-opening percentage of *g*MCC (left) and HCl release (right) in polymer **3** at various sonication time.



**Figure S5.** Ring opening% of *g*DCC and BCOE vs. scission cycles. The slope (or *Φ* value) of linear fitting indicates the activation of mechanophore per chain scission. *g*DCC: *Φ* = 0.48; BCOE: *Φ* = 0.39.



**Figure S6.** *M*n of a **P2** polymer decreased from 83.5 kDa (*Đ* = 1.56) to 43.8 kDa (*Đ* = 1.22) after 60 min ultrasonication treatment, and the *M*n of sonicated **P2** remained nearly unchanged (42.5 kDa, *Đ* = 1.27) after 2d standing time.

### Ultrasonication of **P3** polymer



**Figure S7.** GPC traces of **P3** polymer (left) and corresponding *M*n evolution (right) at various sonication time. GPC analysis was performed immediately after sonication.



**Figure S8.** GPC traces of **P3** polymer (left) and corresponding Mn evolution (right) at various sonication time. GPC analysis was performed after 17d of standing.



**Figure S9.** Molecular weight (MW) analysis of **P3-17d** polymer. The *M*n of high MW peak and oligomer peak were analyzed separately. The theoretical *M*n of high MW fraction at 20 min sonication time was calculated assuming the same scission cycle as **P2** (SC = ln (128.4/81.1)/ln 2 = 0.66). The polymer has broken 2SC-1 = 0.58 times. After one time of chain break, a 120 kDa polymer produces two 60 kDa daughter chains comprised of 39% activated BCOE (Figure SX) along the chain. According to reported method,10 after removal of activated BCOE block, the theoretical *M*n after 0.58 times of chain break is: *M*n = (120\*0.42+2\*60\*0.61\*0.58)/(0.42+0.58\*2) = 58.6 kDa.



**Figure S10.** GPC traces of pristine **P3** polymer at various standing time.

The fraction of lactone relative to incorporated BCOE mechanophore is calculated from the following equations:

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**Figure S11.** 1H-NMR (CDCl3, 500 MHz) spectra stack of sonicated **P3** polymer at various standing time. **P3** polymer was subjected to ultrasonication for 60 min before 1H NMR analysis.



**Figure S12.** HRMS analysis of **P3** polymer after 60 min sonication and further 20 days of standing.

# **SMFS analysis**

## **Determination of the thermal activation energy**

In a 25 mL dry Shlenk flask, 20 mg of BCOE diene derivative **3** was dissolved in 2 mL diphenyl ether. The flask was then heated to 150 oC under N2. Aliquots of 0.1 mL solution at time point (0, 30, 60, 160, 270, 360 min) was took from the flask and dilute with CDCl3 for 1H NMR analysis. Note: Due to the more strained 8-member ring in the ring opened product and presence of THP protecting groups, the ring opened (RO) compound **3** can undergo reversible ring closing to give pristine ring closed (RC) form without producing lactone.11-12

The percentage of ring closed from in the system can be calculated using the following equation:

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**Figure S13.** 1H NMR (CDCl3, 500 MHz) spectra stack of compound **3** in diphenyl ether after heated at 150 oC for various time.



**Figure S14.** Percentage of ring closed form over time at 150 oC in diphenyl ether.

The equilibrium at 150 oC can be estimated from the plateau (33%) of fitting:

The observed rate constants is: kobs = k1 – k-1 = 1.132×10-2 min-1

Therefore, the ring-opening rate constant is: k1 = 2k-1 = 2kobs = 2.264×10-2 min-1 = 3.77×10-4 s-1

According to the transition state theory, the thermal activation energy can be estimated:

Mechanically induced disrotatory ring opening of BCOE is a forbidden pathway. Hence, the activation energy of forbidden reaction would be at least 4 kcal/mol more than thermal allowed path way.13 The activation energy of disrotatory ring opening of BCOE is:

∆G‡ > 31.7 + 4 kcal/mol = 35.7 kcal/mol

## **SMFS curve analysis**

Force-extension curves of polymer **P1** were analyzed using method reported previously.14 Pre- and post- transition force curves were fitted with extended freely jointed chain (FJC) model to give the contour lengths of polymers before and after transition. Further analysis with Bell-Evans (BE) or Cusp models provided ∆x‡ information.



**Figure S15.** Fitting of pre and post transition in force-extension curve with extended FJC model. The contour before and after transition are obtained: before, Li = 249.9 nm; after, Lf = 271.5 nm.



**Figure S16.** Fitting of force-extension curve with BE model. Mechanical coupling ∆x‡ = 0.87 Å.



**Figure S17.** Fitting of force-extension curve with Cusp model. Mechanical coupling ∆x‡ = 1.06 Å.

## **Additional SMFS curves**









**Table S1.** List of results from SMFS curves analysis

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| # | Li nm | Lf nm | Lf/Li | Kuhn length (nm) | K1 (pN/nm) | K2 (pN/nm) | Δx‡ | | F\* (pN) |
| BE | Cusp |
| 1 | 99.5 | 105.0 | 1.056 | 0.225 | 7.51×104 | 8.31×104 | 0.94 | 1.15 | 1539 |
| 2 | 186.8 | 190.4 | 1.020 | 0.237 | 7.43×104 | 6.50×104 | 0.94 | 1.15 | 1557 |
| 3 | 198.4 | 209.7 | 1.057 | 0.279 | 6.45×104 | 8.19×104 | 0.91 | 1.11 | 1594 |
| 4 | 308.1 | 330.3 | 1.072 | 0.355 | 3.80×104 | 5.36×104 | 0.92 | 1.13 | 1529 |
| 5 | 339.2 | 360.9 | 1.064 | 0.288 | 6.20×104 | 8.01×104 | 0.84 | 1.03 | 1690 |
| 6 | 249.9 | 271.5 | 1.086 | 0.316 | 5.03×104 | 9.61×104 | 0.87 | 1.06 | 1645 |
| 7 | 465.6 | 495.2 | 1.064 | 0.251 | 6.99×104 | 9.87×104 | 0.84 | 1.03 | 1690 |
| 8 | 367.5 | 395.7 | 1.077 | 0.283 | 5.85×104 | 9.27×104 | 0.82 | 1.01 | 1716 |
| 9 | 138.9 | 147.7 | 1.063 | 0.199 | 1.12×104 | 1.53×104 | 0.93 | 1.14 | 1566 |
| 10 | 265.6 | 280.5 | 1.056 | 0.298 | 5.57×104 | 8.49×104 | 0.85 | 1.04 | 1704 |
| 11 | 129.6 | 139.8 | 1.078 | 0.263 | 6.45×104 | 9.78×104 | 0.92 | 1.13 | 1570 |
| 12 | 89.6 | 95.5 | 1.066 | 0.308 | 5.46×104 | 7.48×104 | 0.90 | 1.10 | 1609 |
| Avg. |  |  | 1.063 |  |  |  | 0.89 | 1.09 | 1617 |
| SD. |  |  | 0.017 |  |  |  | 0.04 | 0.05 | 68 |
| **Report** |  |  | **1.063**  **±0.017** |  |  |  | **0.89**  **±0.04** | **1.09**  **±0.05** | **1620**  **±70** |

# **CoGEF modeling**

CoGEF modeling of BCOE repeating unit and corresponding forbidden ring opening product were performed on Spartan’16 V2.0.7 version at Molecular Mechanics/MMFF theory level. The end-to-end distance was constrained and relaxed with step interval of 0.1 Å. The obtained energy at each relaxed step was plotted as a function of distance. Further quadratic fitting and subsequent analysis from the first derivative gave force vs. extension relation, from which the contour length (x0) at zero force can be extrapolated.

## **End-to-end distance modeling of ring closed BCOE**





**Figure S18.** Quadratic fit of energy vs. distance curve (blue); force vs. distance plot (orange). End-to-end distance of ring closed BCOE: x0 = 13.846 Å.

## **End-to-end distance modeling of ring opened BCOE**





**Figure S19.** Quadratic fit of energy vs. distance curve (blue); force vs. distance plot (orange). End-to-end distance of ring closed BCOE: x0 = 16.022 Å.

The ratio of final contour length (Lf) to initial contour length (Li) can be calculated:

*x* is the incorporation percentage of BCOE; *l*COD is the contour length of epoxy-COD repeating unit.15

# **NMR spectra**

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1H NMR (CDCl3, 500 MHz) spectrum of compound **1**. “\*” labeled peak is from unreacted 2-butyne-1,4-diol.

A picture containing sky

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13C NMR (CDCl3, 125 MHz) spectrum of compound **1**. “\*” labeled peaks are from unreacted 2-butyne-1,4-diol.



1H NMR (CDCl3, 500 MHz) spectrum of compound **2**.

A close up of a logo

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13C NMR (CDCl3, 125 MHz) spectrum of compound **2**.



1H NMR (CDCl3, 500 MHz) spectrum of compound **3**.



13C NMR (CDCl3, 125 MHz) spectrum of compound **3**.

A close up of a mans face

Description automatically generated

1H NMR (CDCl3, 500 MHz) spectrum of macrocycle **4**.

A picture containing sky

Description automatically generated

13C NMR (CDCl3, 125 MHz) spectrum of macrocycle **4**.



1H NMR (CDCl3, 500 MHz) spectrum of polymer **P1**. The BCOE content is: 1×2/7.67×100% = 28%



1H NMR (CDCl3, 500 MHz) spectrum of polymer **P1**. The BCOE content is: 0.7×2/1×100% = 14%



1H NMR (CDCl3, 500 MHz) spectrum of polymer **P2**. The BCOE content is: 1/(2×3.54)×100% = 14 %

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