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Supporting Material for

Characterizing the Mechanochemically Active Domains in *gem*-Dihalocyclopropanated Polybutadienes under Compression and Tension

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Contents

General Procedures:

Unless otherwise stated, starting materials were obtained from commercial sources and used without further purification. *Cis*-1,4-Polybutadiene (PB) was purchased from Sigma-Aldrich and was composed of ~98 % *cis*-1,4- and ~2 % 1,2-PB.

Gel permeation chromatography analyses were performed with a Varian Prostar Model 210 pump, a Wyatt Dawn EOS multi-angle light scatterer (MALS), Wyatt QELS (quasi-electric light scattering), Wyatt Optilab DSP Interferometric Refractometer (RI), and a series of two Agilent Technology PL gel columns (7.5 X 300mm, 1 79911GP-503 (103Å) and 1 79911GP-504 (104 Å)) in tetrahydrofuran at 22 ^{o}C (room temperature). Molecular weights were calculated by multi-angle light scattering (MALS) gel permeation chromatography (GPC). Refractive index increment (dn dc^{-1}) values were calculated by injecting known amounts of polymer and back-calculating the appropriate values.

Ultrasound experiments were performed in BHT-free tetrahydrofuran on a Vibracell Model VCX500 operating at 20 kHz with a 12.8 mm replaceable tip titanium probe from Sonics and Materials (http://www.sonics.biz/). The sonications were carried out on ~18mL of 1mg/mL polymer solutions in tetrahydrofuran in an ice/water bath of ~6-9 ^{o}C in a 3-necked Suslick vessel. Solutions were deoxygenated with bubbling N_2 for 30 minutes prior to sonication and a positive headspace of N_2 was kept during the experiment. Pulsed ultrasound was carried out at 8.7 W/cm^2 of power at 1s on 1s off. ^{1}H and ^{13}C NMR analyses were conducted on either a 400 MHz or 500 MHz Varian spectrophotometer in $CDCl_3$ and residual solvent peak (7.240 ppm [^{1}H]; 77.23 ppm [^{13}C]) was used as an internal reference. Compression studies were conducted on 70-80 mg of solid polymer in a KBr pellet press and compressed with a Carver Laboratory Press at room temperature. The compressive forces were applied manually, read directly from an attached pressure dial. The cross-sectional area of the polymer sample changed during compression, and at the end of the compression the sample typically filled the pellet press surface area (0.194 inches^{-2}). The pressures reported here were obtained by dividing the applied forces by that area, and they should be regarded as approximate (within a factor of 2-3) lower limits.

The internal diameter of the press was measured as 12.6 mm. Polymers were compressed with a manually driven Carver Laboratory Press and pressures were measured directly off a dial directly connected to the press.

Synthesis

Gem-dichorocyclopropanated polybutadiene (*g*DCC-PB)

411 kDa 98 % *cis-g*DCC-PB (A)

4 g (74.0 mmoles) *cis*-PB and 2.5 g (6.9 mmoles) cetyltrimethylammonium bromide (CTAB) were dissolved in 400 mL $CHCl_3$ and the solution was deoxygenated with bubbling N_2 for 30 minutes. In a separate round bottomed flask was dissolved 21 g (525 mmoles) NaOH in 50 mL DI-H_2O and the solution was deoxygenated with bubbling N_2 for 30 minutes. After each solution was deoxygenated, the NaOH solution was added dropwise by syringe under N_2 to the polymer solution. The reaction was allowed to proceed overnight (~16 hours). After 16 hours the reaction was washed 3X with 1:1 brine:DI-H_2O, rotovapped to minimal volume and the polymer was precipitated with methanol. The polymer was redissolved in CH_2Cl_2, washed 3X with DI-H_2O, rotovapped to minimal volume, precipitated with methanol and dried under vacuum. ^{1}H NMR δ 1.63 ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 65.22, 32.82, 32.72, 32.68, 32.62, 24.49, 24.34, 24.28. MALS-GPC (dn dc^{-1} = 0.1200 mL g^{-1}); M_N = 411,000 g mol^{-1}, M_W = 687,000 g mol^{-1}, PDI = 1.67.

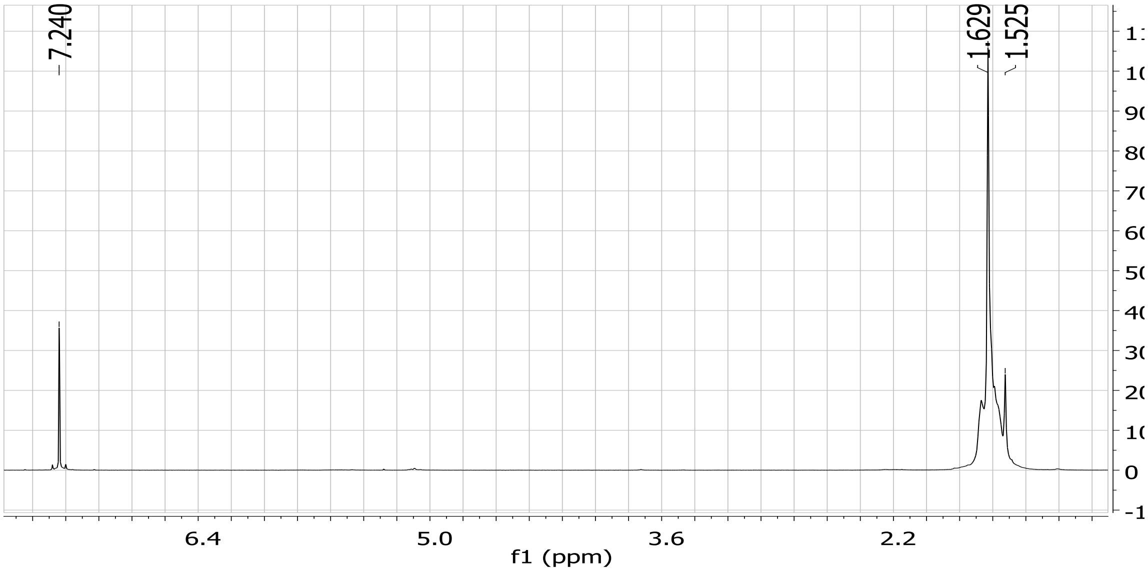


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of >98 % *cis*-*g*DCC polymer.

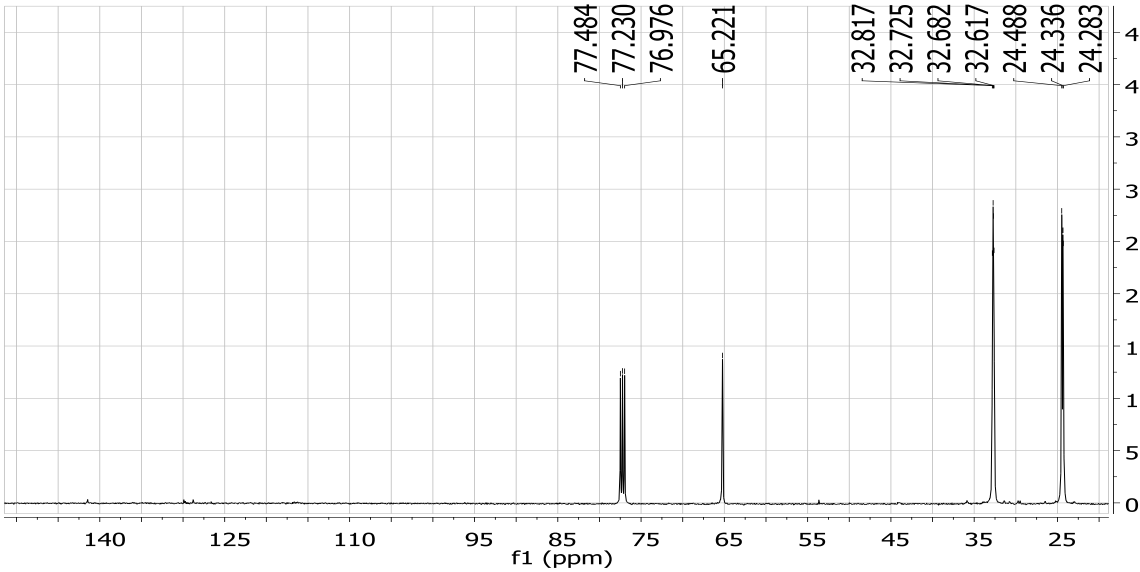
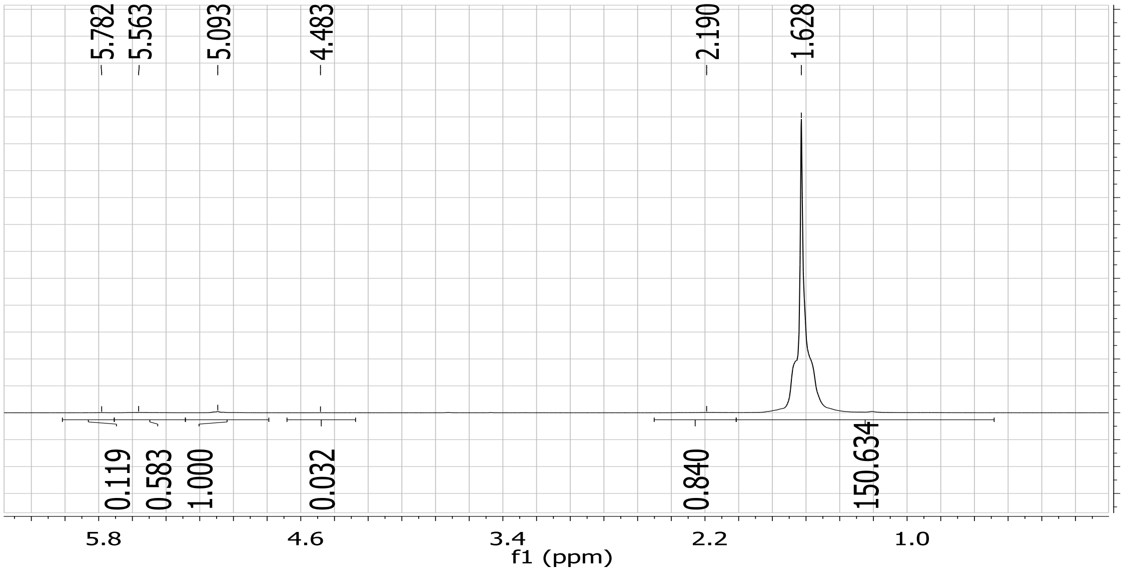


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) of *cis*-*g*DCC-PB.

411 kDa 98 % *cis-g*DCC-PB (B)

5g of *cis*-1,4-PB was functionalized by a similar synthesis to the above described procedure ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (b, 0.12H); 5.56 (b, 0.58H); 5.09 (b, 1.00H); 4.48 (b, 0.03H); 2.19 (b, 0.84H); 1.63 (b, 150.63H). Copolymer composition = 98.3 % *g*DCC; 1.7 % PB. MALS-GPC (dn dc^{-1} = 0.1200 mL g^{-1}): M_N = 411,000 g mol^{-1}; M_W = 565,000 g mol^{-1}; PDI = 1.37.



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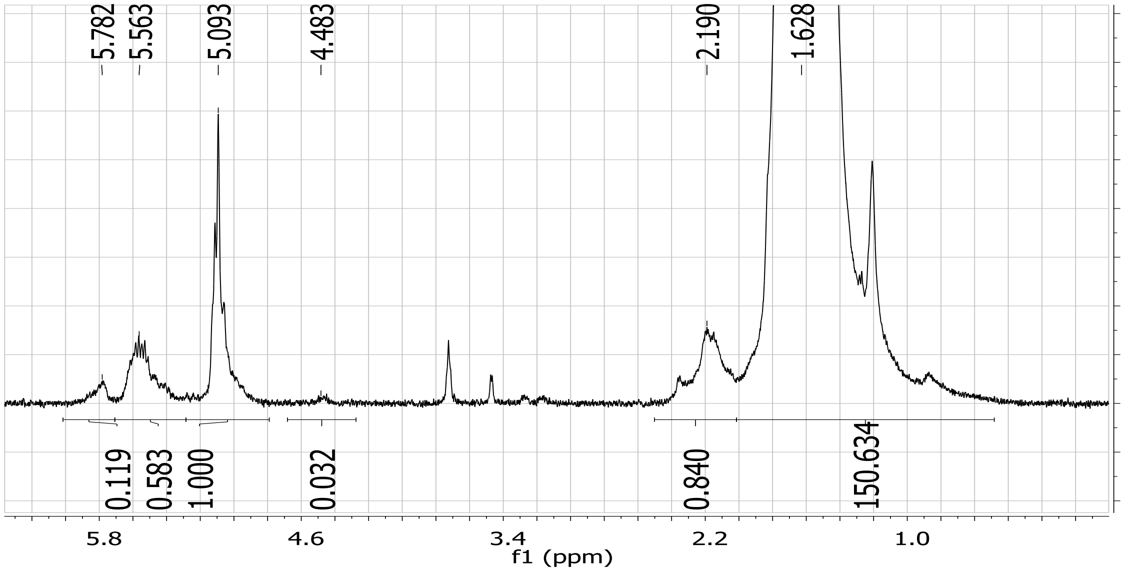

b]

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) normalized vertically [a] and zoomed [b] to show residual PB residues after *cis*-PB functionalization.

Gem-dibromocyclopropanated polybutadiene (*g*DBC-PB)

285 kDa 87 % *cis*-*g*DBC-PB (Compression Studies)

5 g (92.4 mmoles) *cis*-PB and 3.4 g (9.3 mmoles) CTAB were dissolved in ~400 mL CH_2Cl_2. After the polymer had dissolved, 50 mL (572 mmoles) $CHBr_3$ was added and the solution was deoxygenated for 30 minutes with bubbling N_2. In a separate round bottomed flask was dissolved 36 g (900 mmoles) NaOH in 50 mL DI-H_2O and the solution was deoxygenated with bubbling N_2 for 30 minutes. After 30 minutes the NaOH solution was added dropwise to the polymer solution by syringe under N_2 and the reaction was allowed to proceed overnight (~ 16 hours). After 16 hours the reaction was washed 3X with 1:1 brine:DI-H_2O, rotovapped to minimal volume and the polymer was precipitated with methanol. The polymer was redissolved in CH_2Cl_2, washed 3X with DI-H_2O, rotovapped to minimal volume, precipitated with methanol and dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (b, 2.00H); 5.09 (b, 0.24H); 2.28 (b, 4.47H); 1.63 (b, 48.11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.80, 37.31, 36.73, 34.85, 33.56, 27.49, 26.42, 26.27. Polymer composition = 11.3 % 1,4-PB; 1.4 % 1,2-PB; 87.3 % *cis*-*g*DBC. MALS-GPC (dn dc^{-1} = 0.0950 mL g^{-1}); M_N = 285,000 g mol^{-1}, M_W = 508,000 g mol^{-1}, PDI = 1.79.

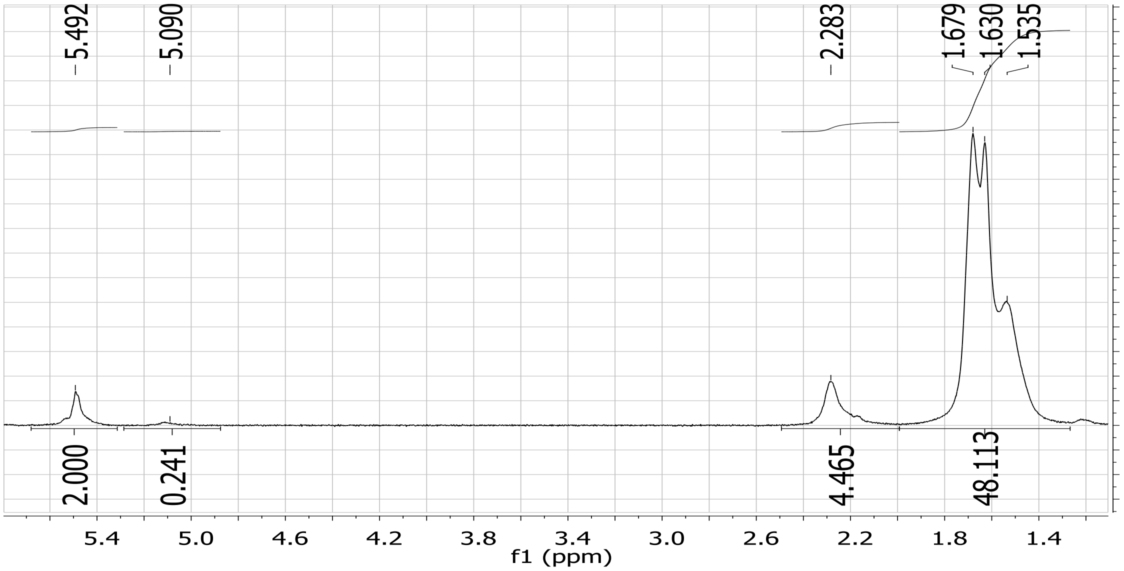

Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of 87 % *cis*-*g*DBC-PB polymer.

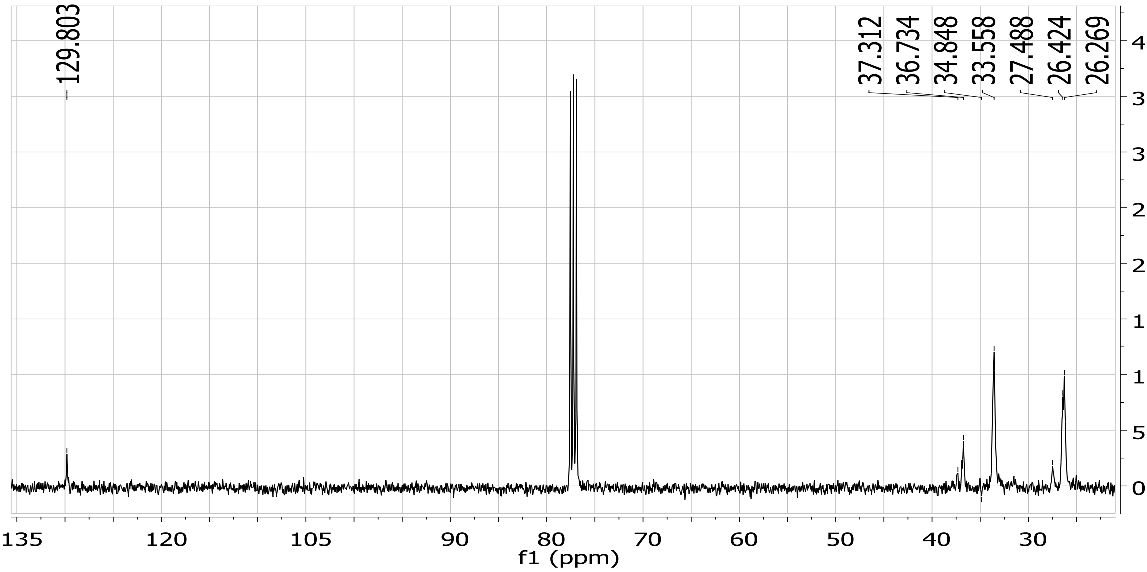

Figure S5. ^{13}C NMR (101 MHz, $CDCl_3$) of 87 % *cis*-*g*DBC-PB. $^{13}CBr_3$ resonances at ~37 ppm.

66 % *cis*-*g*DBC-PB (Tension Experiments)

A similar synthesis to the procedure above was completed. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (b, 2.00H); 5.00 (b, 0.14H); 2.25 (b, 4.19H); 1.60 (b, 12.98H). Copolymer composition = 66.5 % *g*DBC; 33.5 % PB. No molecular weight was determined.

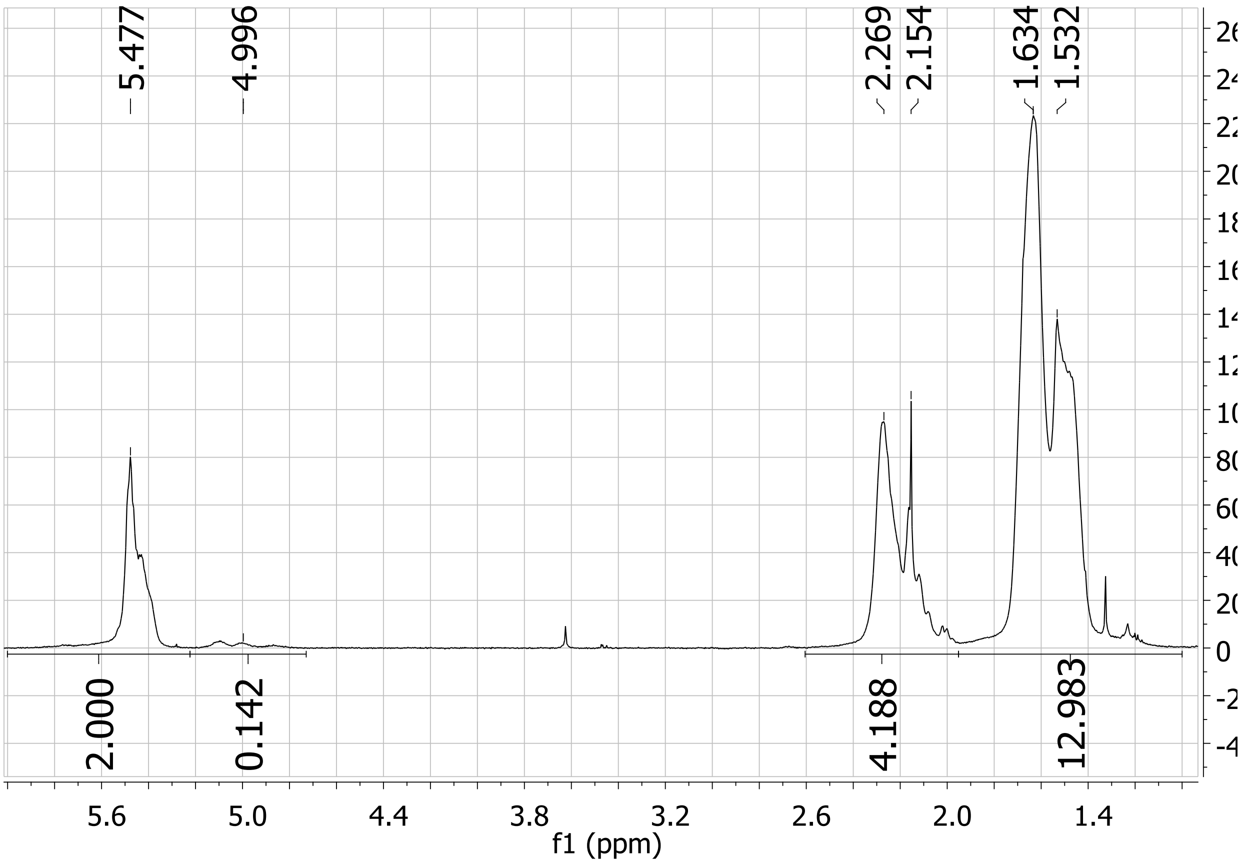

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of 66 % *cis*-*g*DBC-PB copolymer used in tension experiments.

Gem-bromochlorocyclopropanated polybutadiene (*g*BCC-PB)

559 kDa 80 % *cis-g*BCC-PB

5.80 g (107 mmoles) *cis*-PB, 41.2 mL (485 mmoles) $CHBr_2Cl$ and 3.95 g (10.9 mmoles) cetyltrimethylammonium bromide were dissolved in 300 mL CH_2Cl_2 and deoxygenated with bubbling $N_2$for 30 minutes. In a separate round bottomed flask was dissolved 42.4 g (1,060 mmoles) NaOH in 100 mL. The solution was allowed to cool to room temperature and deoxygenated with bubbling N_2 for 30 minutes. After the NaOH solution was deoxygenated, the NaOH solution added to the PB solution dropwise under N_2 and the reaction was allowed to proceed overnight (~16 hours). After 16 hours the reaction was washed 3X with DI-H_2O and the polymer was precipitated with methanol. The polymer was reprecipitated twice more with methanol from CH_2Cl_2 and dried on vacuum at room temperature. ^1H NMR (400 MHz, $CDCl_3$) 5.47 (b, 2.00H); 5.06 (b, 0.20H); 2.26 (b, 4.52H); 1.62 (b, 29.57H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.76, 68.17, 65.25, 55.25, 55.13, 54.91, 54.76, 54.64, 49.65, 49.18, 33.49, 33.38, 33.31, 33.12, 33.05, 32.74, 27.57, 27.39, 26.58, 26.43, 26.29, 25.82, 25.22, 24.37, 24.22. Polymer composition = 17.8 % 1,4-PB; 2.1 % 1.2-PB; 80.1 % *cis-g*BCC. MALS-GPC (dn dc^{-1} = 0.1100 mL g^{-1}); M_N = 559,000 g mol^{-1}, M_W = 999,000 g mol^{-1}, PDI = 1.79.

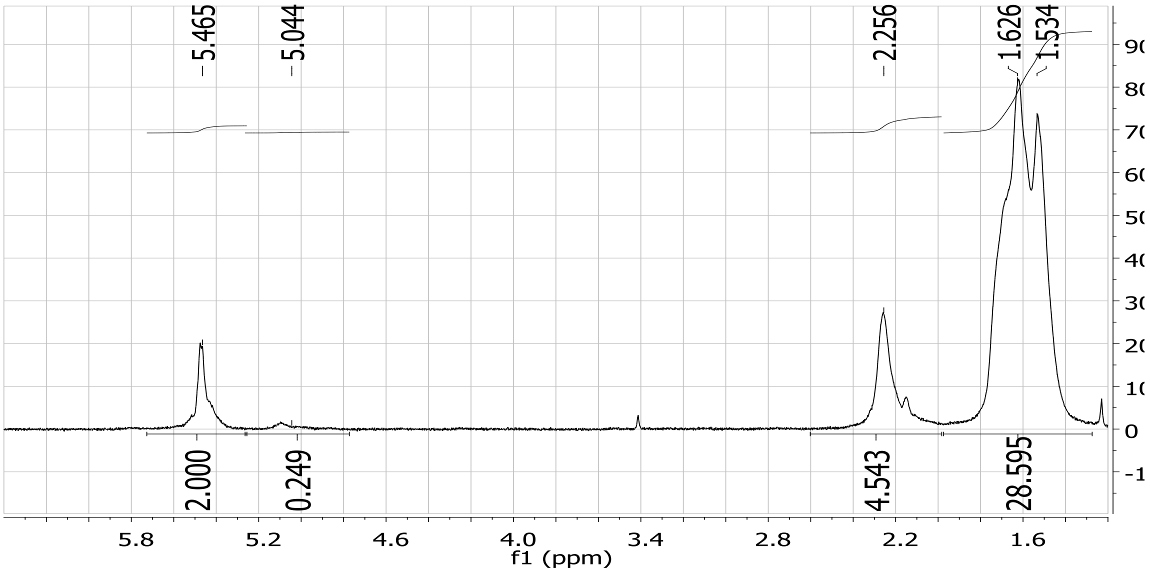

Figure S7. ^1H NMR (400 MHz, $CDCl_3$) of 80 % *cis-g*BCC-PB.

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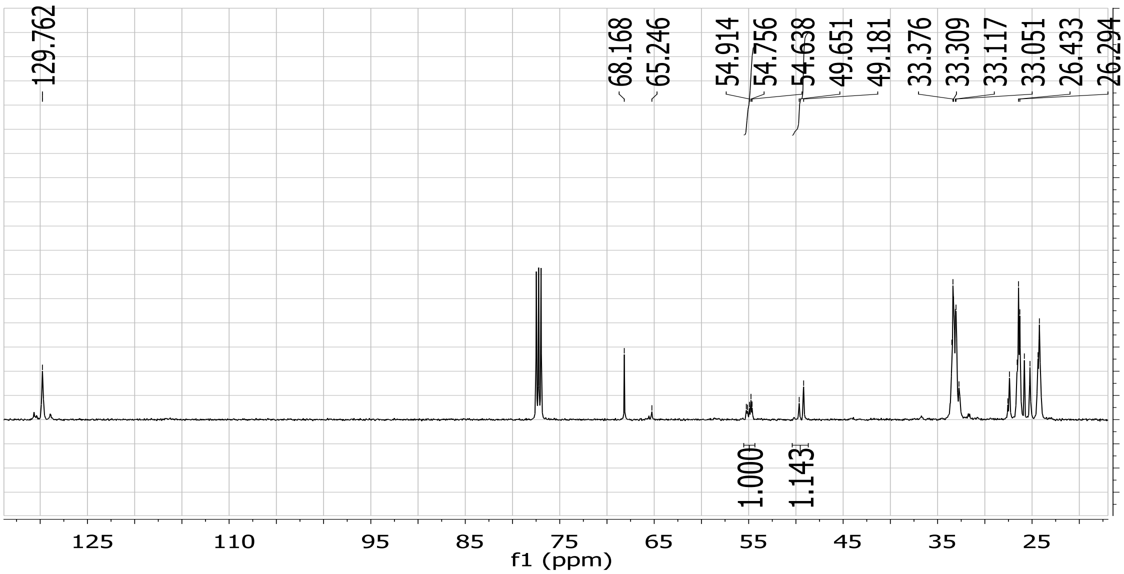


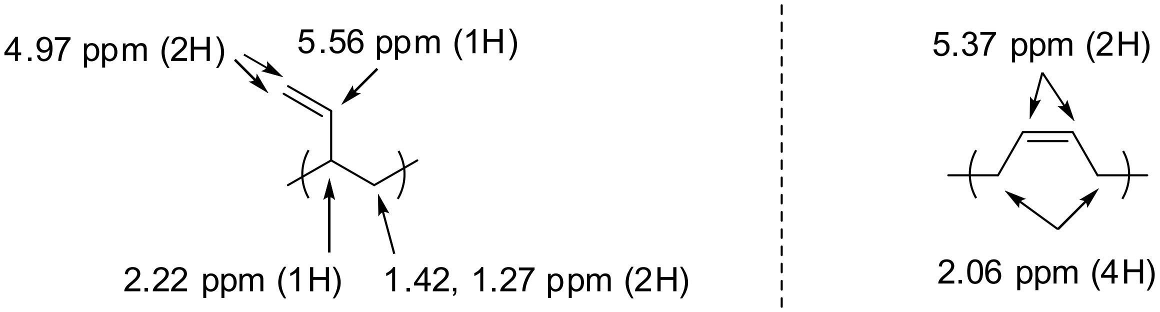
Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) of 80 % *cis-gBC*C-PB. *cis-syn*-Br isomer = 54.8 ppm; *cis-syn*-Cl isomer = 49.5 ppm. Residual THF observed at 68.2 ppm.

Calculations

Polymer Percent Functionalization

The extent of mechanophore addition to *cis*-1,4-PB was conducted in the following manner.

A] The polymer is initially composed of *cis*-1,4-PB and 1,2-PB 'monomer' repeat units. The relevant chemical shifts of these components are:



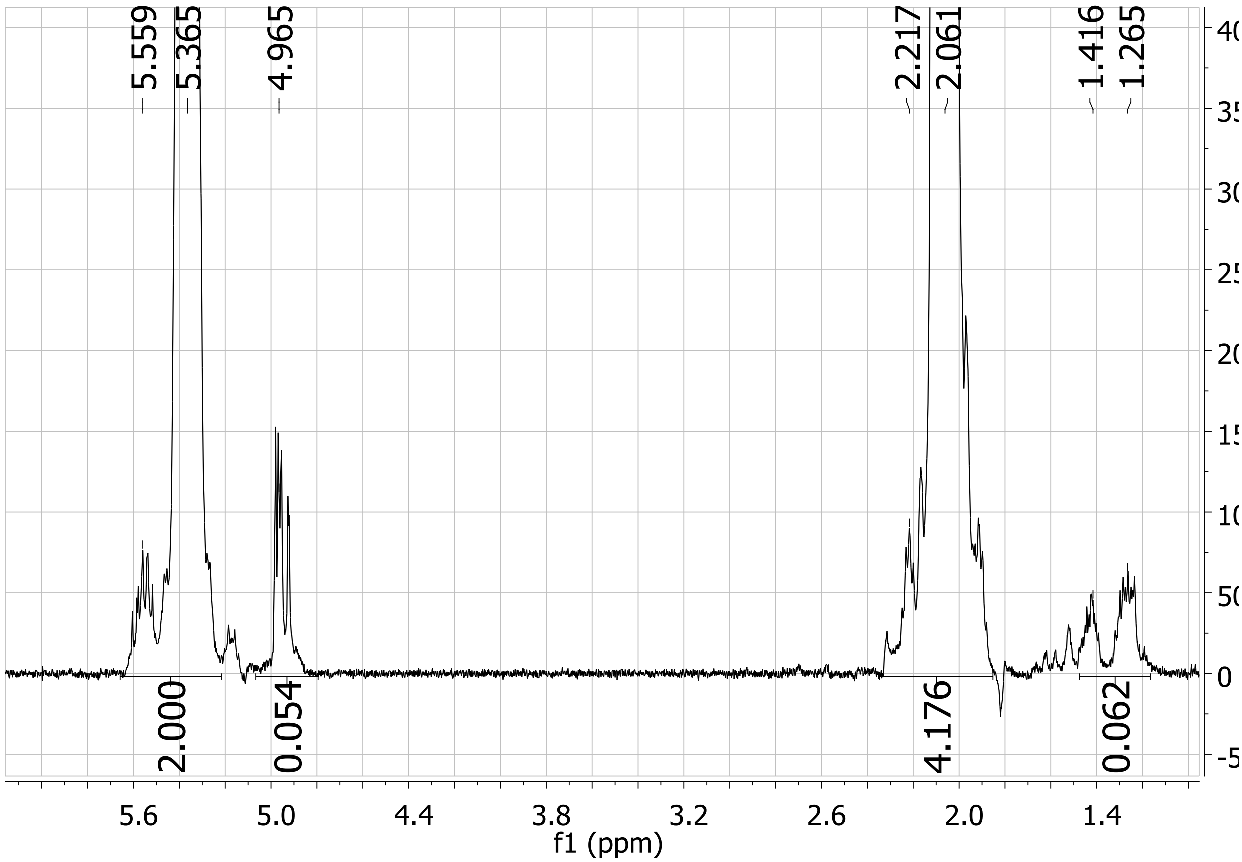
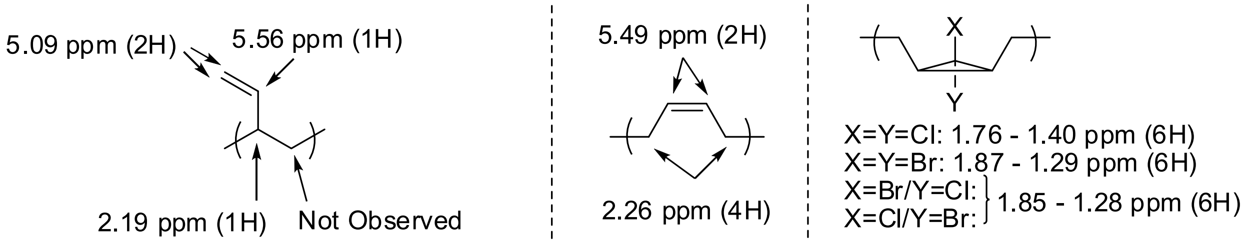


Figure S9. Initial ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 98 % *cis*-1,4-PB.

B] After addition of dihalocarbene, the following chemical shifts are observed for *g*DHC addition products:



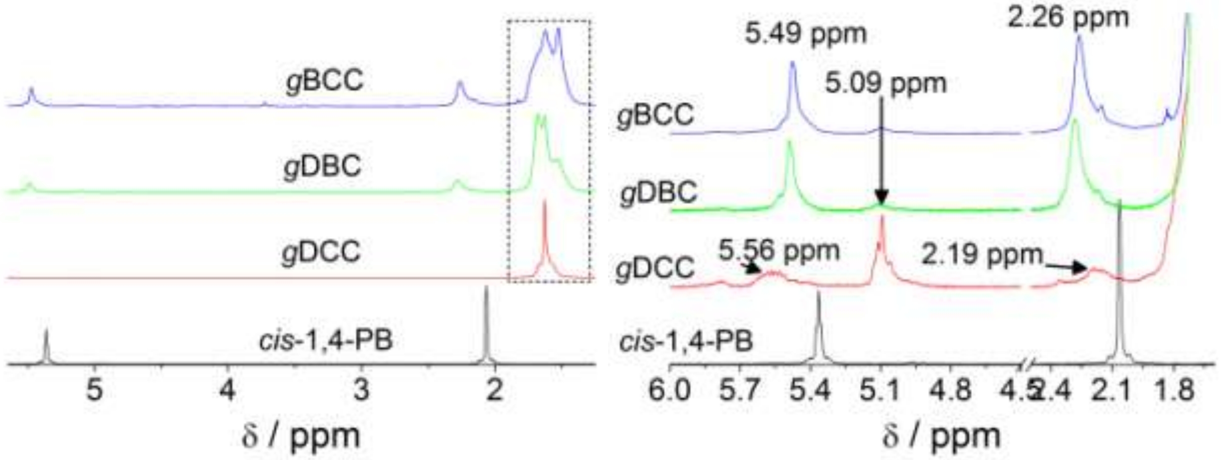


Figure S10. ^{1}H NMR spectra (400 MHz, 1,4-PB / 500 MHz, *g*DHCs; $CDCl_3$) of initial polymers after functionalization of *cis*-1,4-PB with dihalocarbene. *gem*-dihalocyclopropanes are observed at ~ 1.9 – 1.3 ppm as broad multiplets. Graph at right shows zoomed region of the spectra identifying resonances of PB after functionalization of the polymer with dihalocarbene.

C] After functionalization the polymer ^{1}H NMR spectra were recorded and relevant resonances were integrated.

i] *g*DCC polymer: Resonances are observed at the following peaks and intensities.

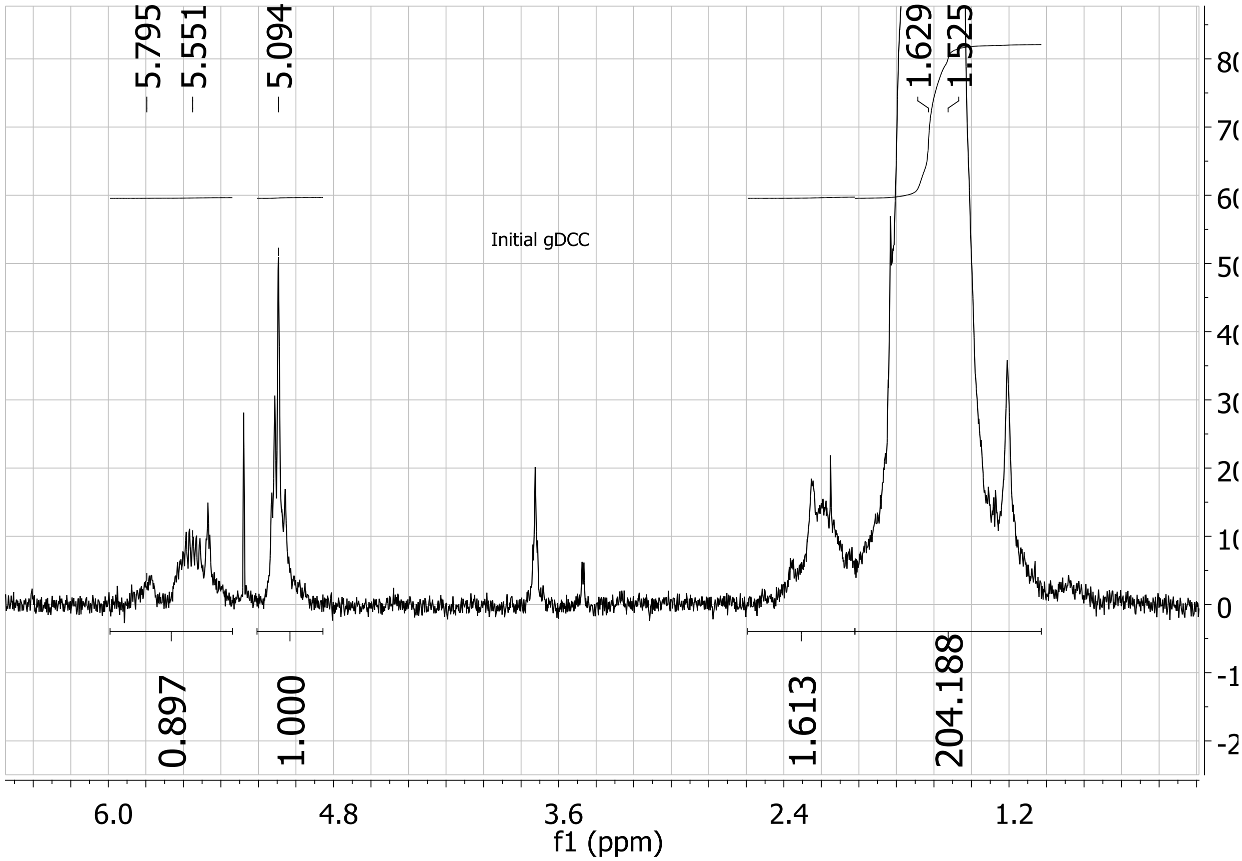


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) of *g*DCC polymer A.

The number of 1,4-PB resonances are thus the calculated from the following equation:

Sum [5.9ppm→5.4 ppm + 2.25 ppm – 5.10 ppm] ÷ 6 protons = [.897+1.613-1]÷6 **= 0.25**

The number of 1,2-PB resonances are thus calculated from the following equation:

[5.10 ppm] ÷ 2 protons = [1.0] ÷ 2 = **0.50**

The number of *g*DCCs are thus calculated from the following equation:

Sum [1.6 ppm – 5.1 ppm] ÷ 6 protons = [204.19 – 1] ÷ 6 = **33.9**

The as calculated numbers indicate the relative ratios of repeat units along the polymer chain and lead to the quantification the polymer structure as 1,4:1,2:*g*DCC = 1:2:136; the *g*DCC content of the polymer is thus ~ 98 % *g*DCC.

From MALS-GPC (dn dc^{-1} = 0.1200 mL g^{-1}), M_N = 411,000 g mol^{-1}. Given the proportions of PB : *g*DCC components of the polymer, the average molecular weight of a 'monomer' unit is [0.02*54.06 g mol^{-1}] + [0.98*137.01 g mol^{-1} = 135.35 and the degree of polymerization (DP) of the polymer is the $M_N \div FW_{AVG}$ = 3037. From the composition of the polymer we then calculate that an average polymer chain is composed of 0.98*3037 = 2976 *g*DCC and 61 PB monomers. [Similar analyses were conducted for the *g*DBC and *g*BCC polymers.]

Percent Ring Opening

The extent of ring opening was monitored by setting the 1,2-PB resonances during ^{1}H NMR integration as a *constant*. We justify the setting of an internal standard since the application of mechanical stress to PB polymers has no transformative affect on these PB values. Thus, the following methodology was developed towards quantifying ring opening in the *g*DHC polymers during compressive stress.

i] From the above analysis we found that when setting the 1,2-PB resonance at 5.10 ppm equal to **1.00**, the number of *g*DCCs was calculated to be **33.9**. Thus, the ring opening percent during compressive activation was calculated by setting the 5.10 ppm resonance to 1.00, integrating the product 2,3-dichloroalkene resonances at ~5.9 ppm and 4.5 ppm, and dividing the average of these two integrations by 29.2; multiplying by 100 to obtain the % ring opening. The average of the integrated values at 5.9 ppm and 4.5 ppm was used since the positions of these resonances are the sum of 2 protons, taking the average of the values implicates the presence of a *single* ring opened *g*DCC.

ii] Example: *g*DCC polymer subjected to compressive stress (178 MPa; 4 polymer folds).

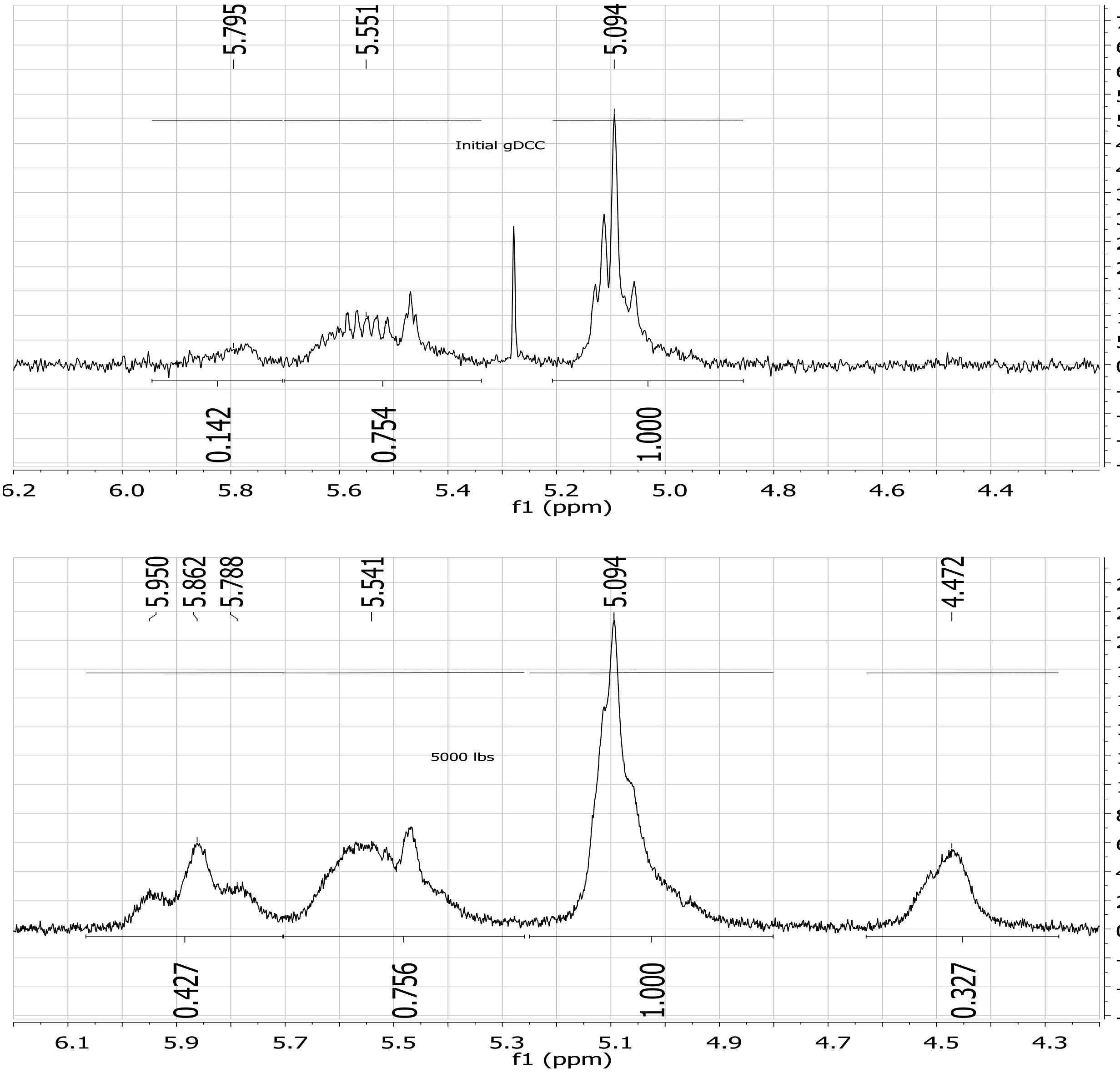


Figure S12. Zoomed ^{1}H NMR spectra of the intial (top) *g*DCC polymer and the *g*DCC polymer subjected to 178 MPa of pressure and 4 polymer folds.

% Ring opening = {[0.427-.142]+[327}÷2 = 0.306 ÷ 33.9*100 = 0.9 % ring opening.

Similar analyses were conducted to determine the extents of ring opening for *g*DBC and *g*BCC polymers.

Pulsed Ultrasound

411 kDa 98 % *cis*-*g*DCC-PB

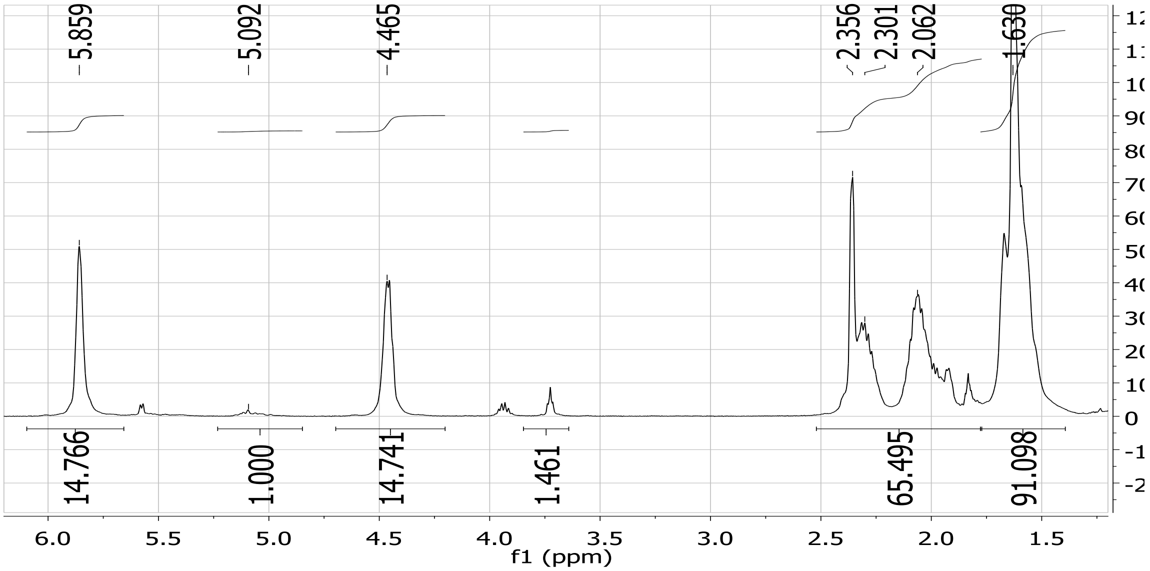


Figure S13. ^{1}H NMR obtained after sonication (10 minutes sonication, THF, 6-9 °C, 6.3 W cm^{-2}, N_2) of *cis*-*g*DCC-PB leads to the formation of resonances (5.86 ppm, 4.47 ppm, 2.5-1.8 ppm) consistent with the formation of 2,3-dichloroalkenes as a result of the electrocyclic ring opening of *cis*-*g*DCC. After 10 minutes M_N = 149 kDa, M_W = 177 kDa. Residual THF is observed at 3.73 ppm and 1.83 ppm.

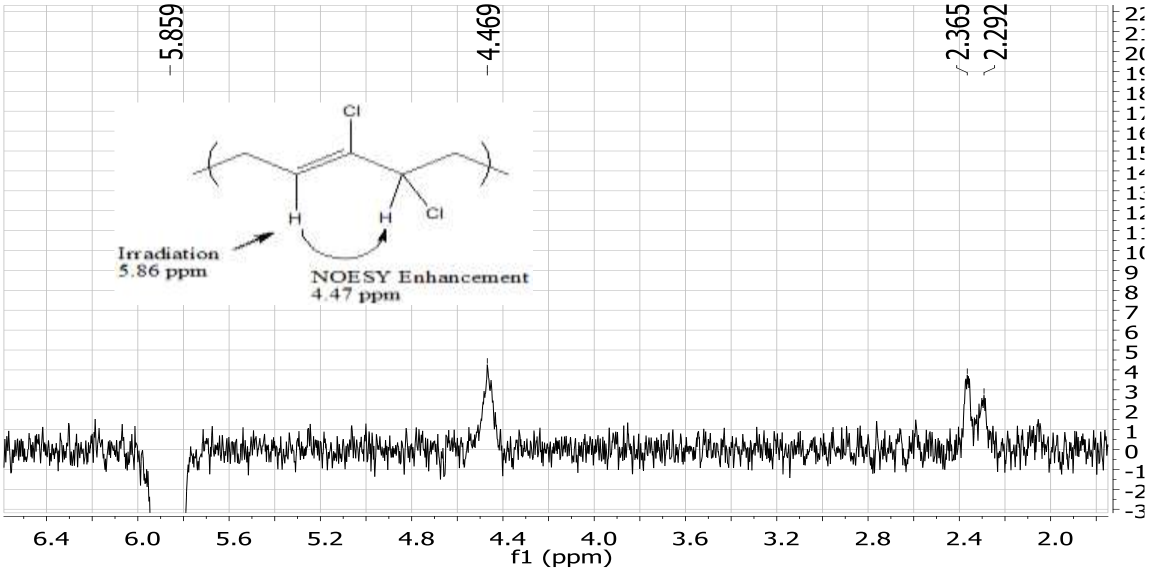


Figure S14. 1D NOESY (400 MHz, $CDCl_3$) of sonicated *g*DCC-PB indicates the (*Z*) stereochemistry of the alkene.

285 kDa 87 % *cis*-*g*DBC-PB

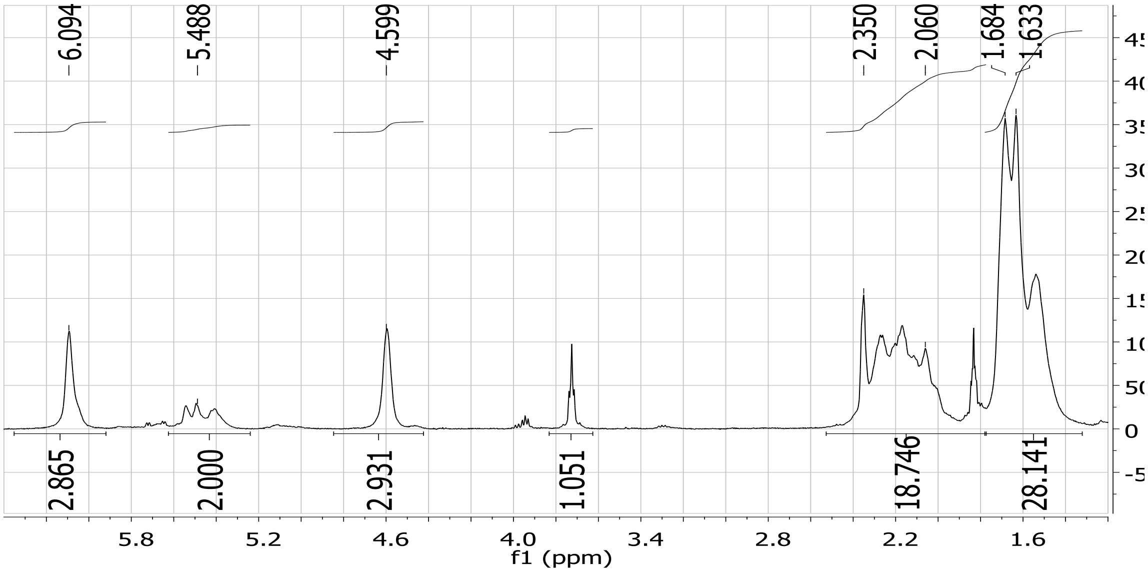


Figure S15. ^{1}H NMR obtained after sonication (10 minutes sonication, THF, 6-9 ^{o}C, 6.3 W cm^{-2}, N$_2$) of *cis*-*g*DBC-PB leads to the formation of resonances (6.09 ppm, 4.60 ppm, 2.5-1.8 ppm) consistent with the formation of 2,3-dibromoalkenes as a result of the electrocyclic ring opening of *cis*-*g*DBC. After 10 minutes M$_N$ = 216 kDa, M$_W$ = 269 kDa. Residual THF is observed at 3.73 ppm and 1.83 ppm.

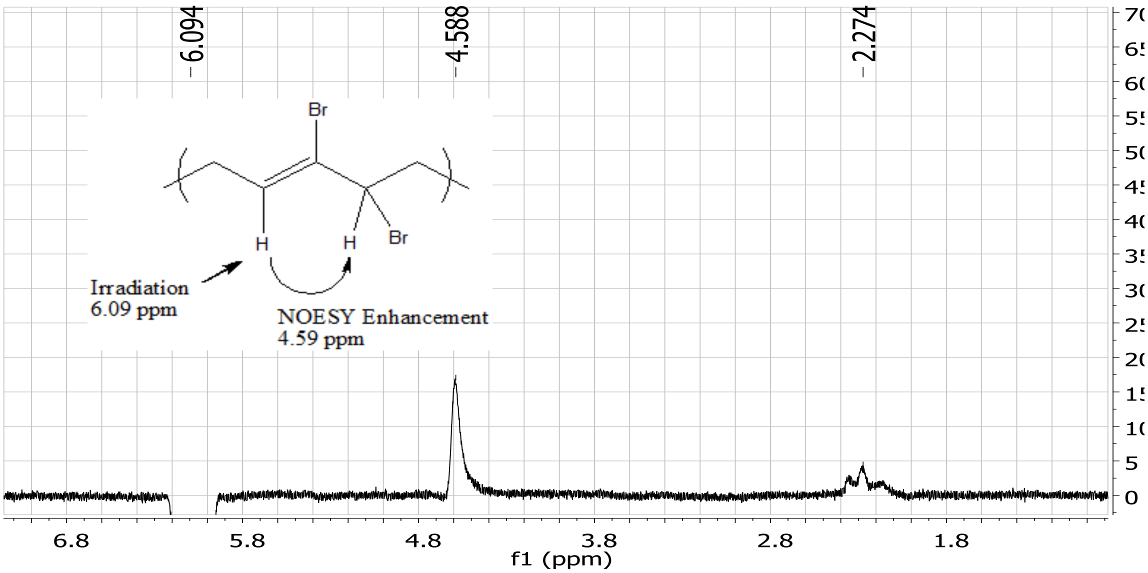
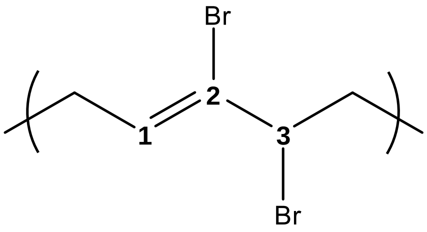


Figure S16. 1D NOESY (500 MHz, CDCl$_3$) of sonicated *g*DBC-PB indicates the (*Z*) stereochemistry of the alkene.



1,2: 137 ppm - 127 ppm

3 : 57.1 ppm

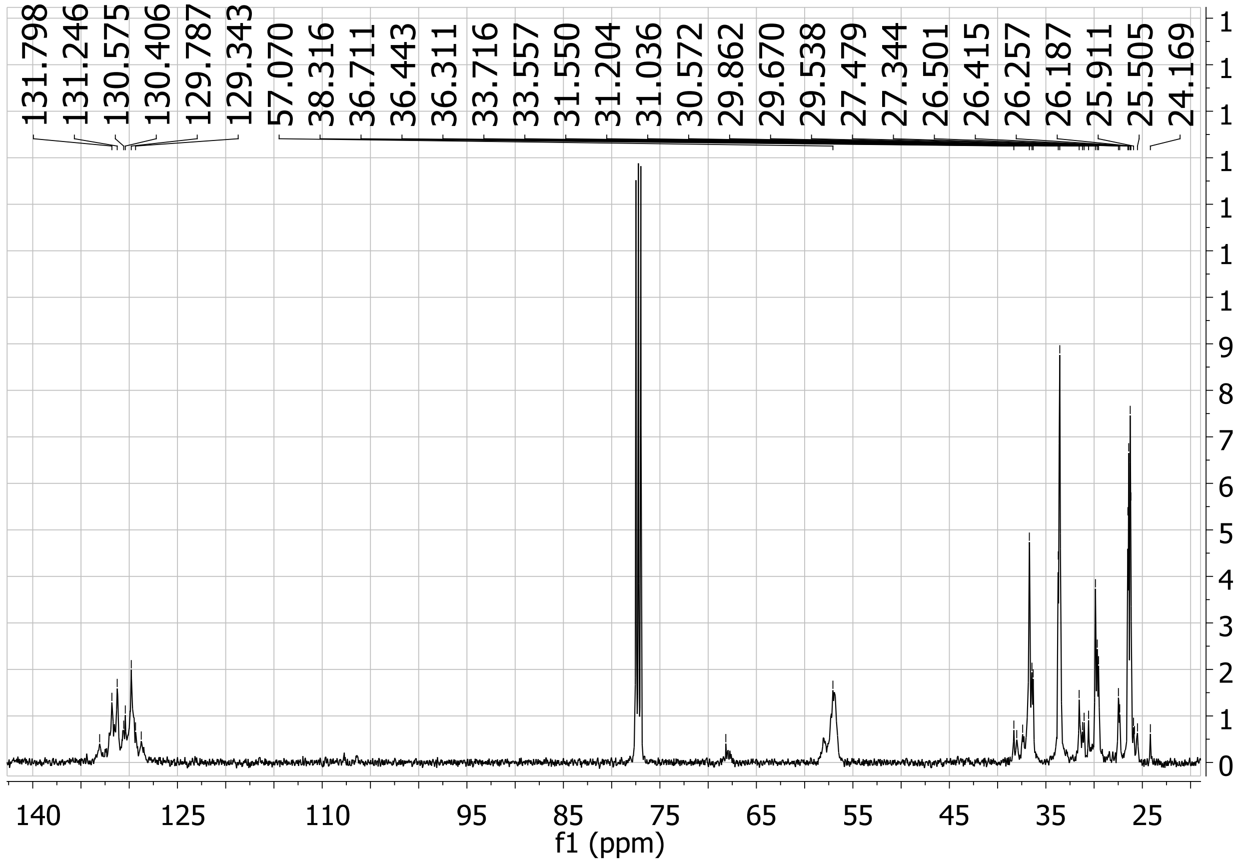


Figure S17. ^{13}C NMR (126 MHz, CDCl$_3$) of sonicated *cis*-*g*DBC-PB. [^{13}C NMR (126 MHz, cdcl$_3$) δ 133.06, 131.80, 131.25, 130.57, 130.41, 129.79, 129.34, 128.75, 68.17, 57.07, 38.32, 38.02, 37.40, 36.71, 36.44, 36.31, 33.72, 33.56, 31.55, 31.20, 31.04, 30.57, 29.86, 29.67, 29.54, 27.48, 27.34, 26.50, 26.41, 26.26, 26.19, 25.91, 25.82, 25.51, 24.17.]

559 kDa 80 % *cis*-*g*BCC-PB

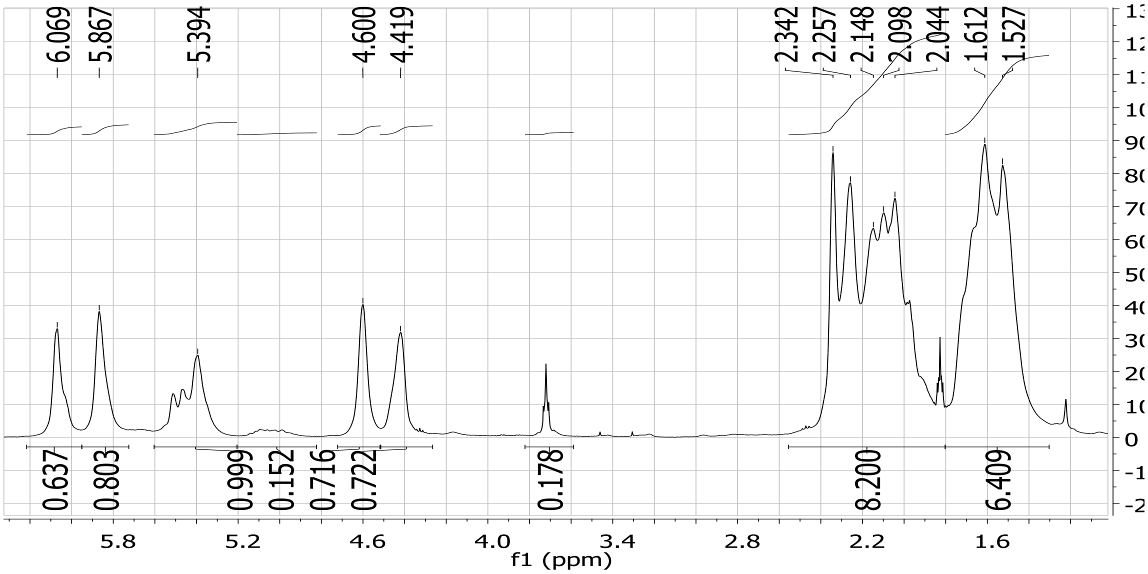


Figure S18. ^{1}H NMR obtained after sonication (10 minutes sonication, THF, 6-9 ^{o}C, 6.3 W cm^{-2}, N_2) of *cis*-*g*BCC-PB leads to the formation of resonances (6.09 ppm, 5.88 ppm, 4.61 ppm, 4.43 ppm, 2.5-1.8 ppm) consistent with the formation of both 2-bromo-3-chloro- and 2-chloro-3-bromoalkene products as a result of the electrocyclic ring opening of both isomers of *cis-gBC*C. After 10 minutes M_N = 165 kDa, M_W = 205 kDa. Residual THF is observed at 3.73 ppm and 1.83 ppm.

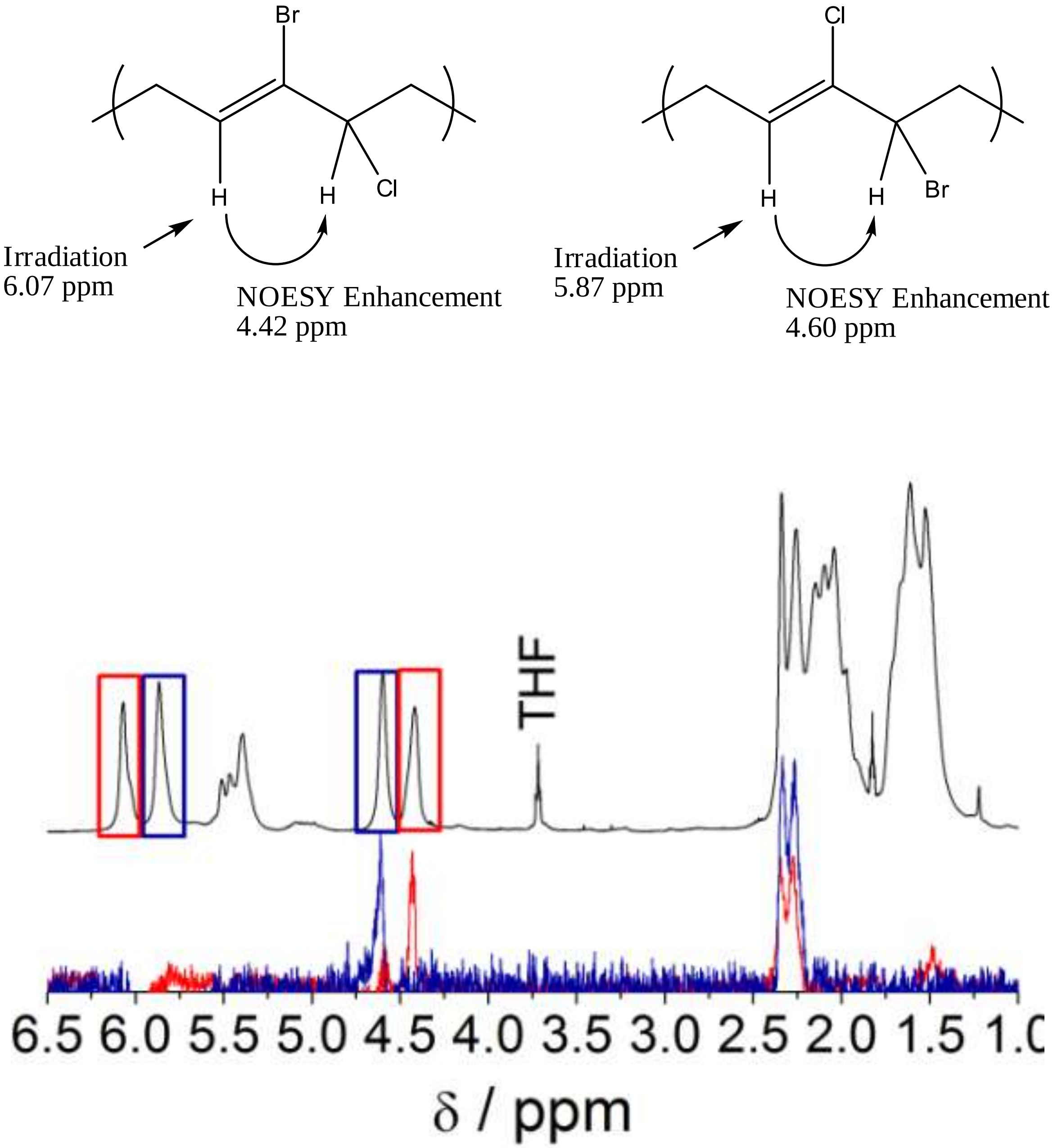
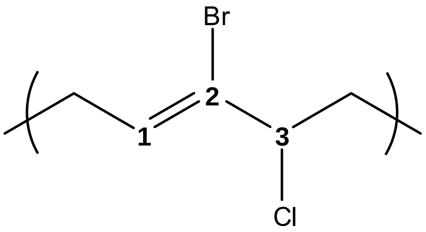
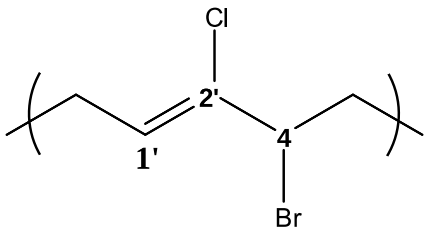


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$, top spectrum) after sonication of *gBC*C-PB (top) and 1D NOESY spectra following excitation at 6.069 ppm (red) and 5.867 ppm (blue) indicate the (Z) stereochemistry of each product.



1,2: 137 ppm - 127 ppm

3 : 65.2 ppm



1',2': 137 ppm - 127 ppm

4 : 55.4 ppm

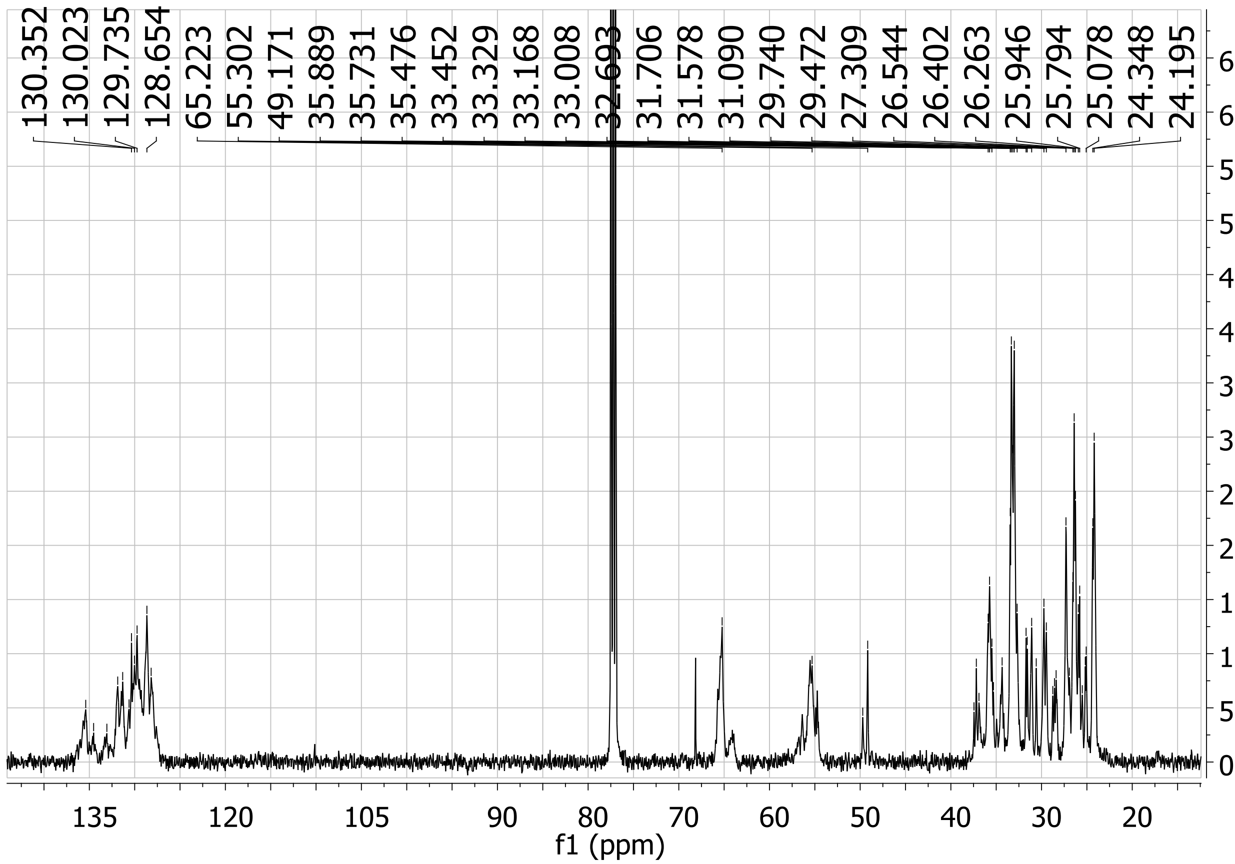
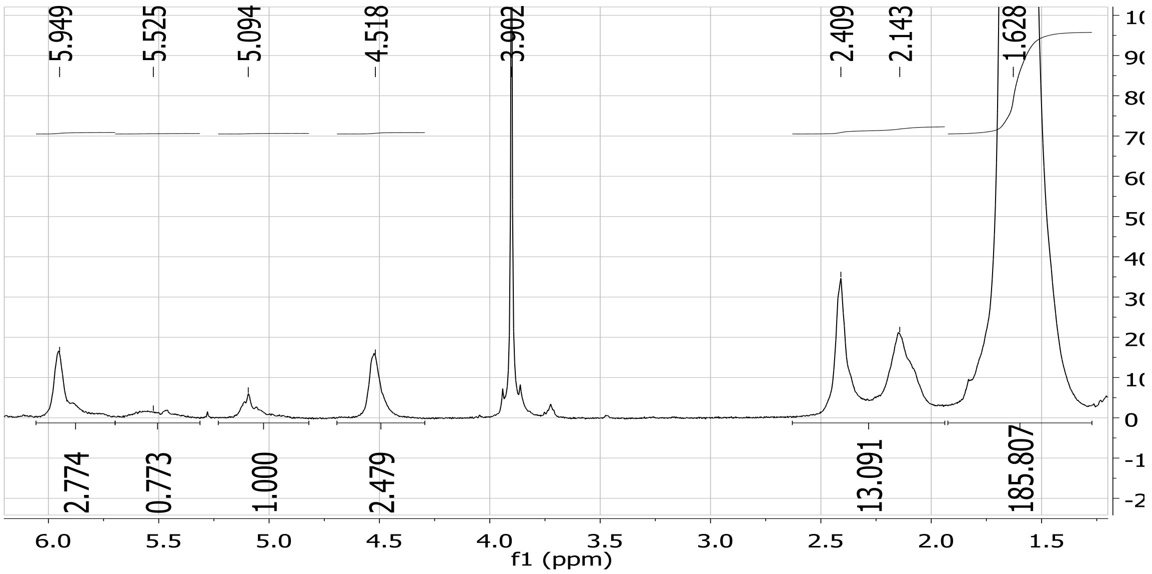


Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$) after sonication of *gBC*C-PB. [^{13}C NMR (126 MHz, $cdcl_3$) δ 135.40, 134.53, 133.07, 131.87, 131.32, 130.62, 130.35, 130.02, 129.74, 128.65, 128.18, 65.22, 55.30, 49.72, 49.17, 37.45, 37.19, 36.90, 35.89, 35.73, 35.48, 35.30, 34.35, 33.45, 33.33, 33.17, 33.01, 32.69, 31.71, 31.58, 31.09, 30.58, 29.74, 29.47, 28.76, 28.57, 28.39, 27.31, 26.93, 26.54, 26.40, 26.26, 25.95, 25.79, 25.51, 25.18, 25.08, 24.35, 24.19.]

Thermolysis

411 kDa 98 % *cis*-*g*DCC-PB



b]

Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) after thermolysis (185 °C, methyl benzoate, N_2, 17 hours) indicates the thermal ring opening of *g*DCC to 2,3-dichloroalkene (5.95 ppm, 4.52 ppm).

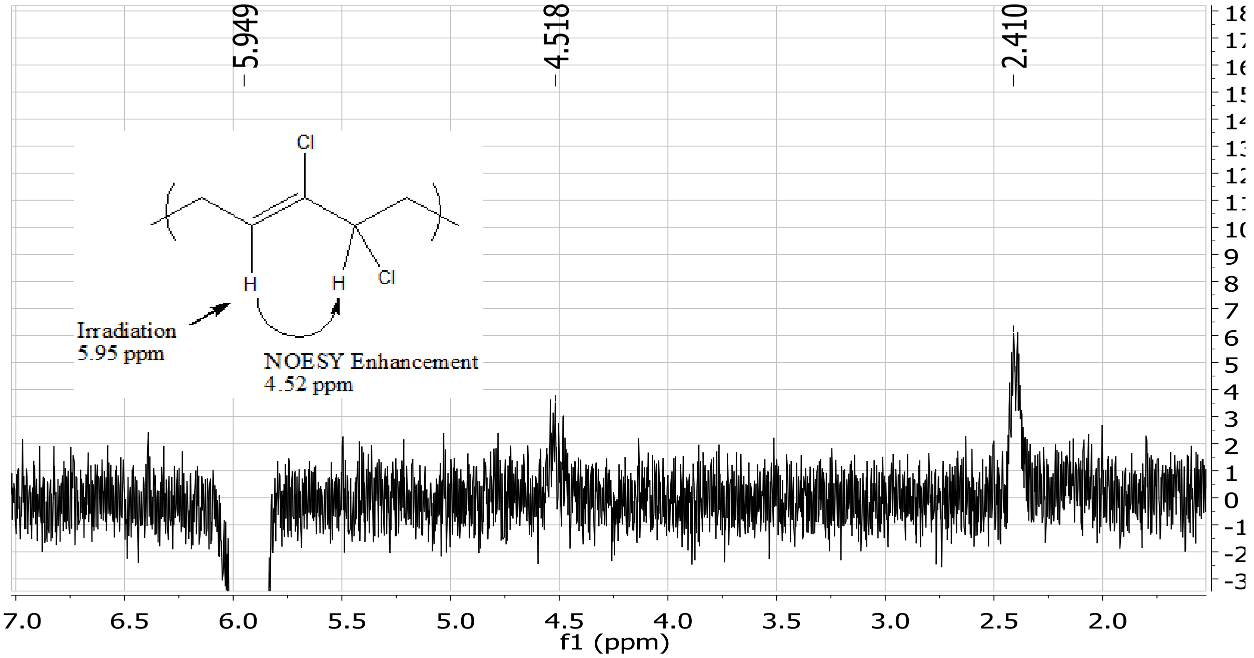


Figure S22. 1D NOESY (500 MHz, $CDCl_3$) of thermalized *g*DCC-PB indicates the (*Z*) stereochemistry of the alkene.

285 kDa 87 % *cis-g*DBC-PB

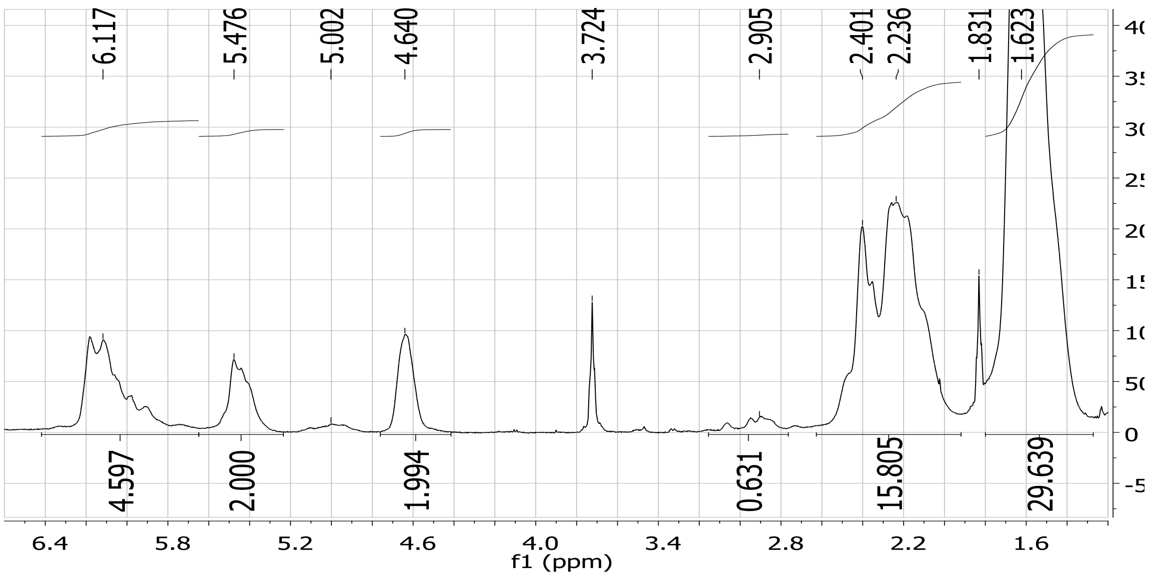
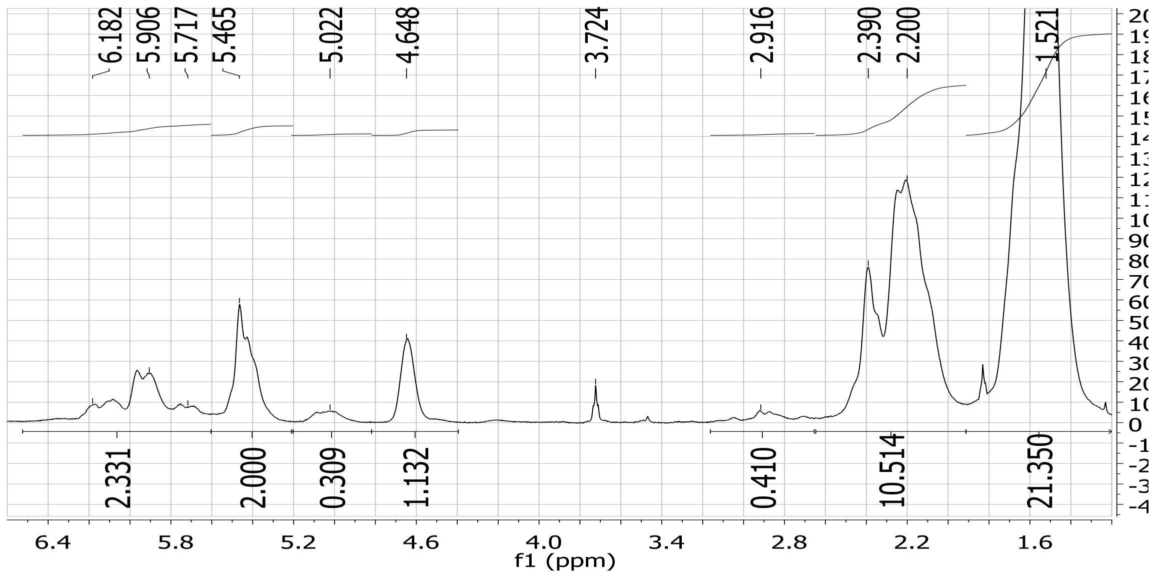


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) after thermolysis of *g*DBC polymer (165 °C, 17 hours methyl benzoate, N_2) indicates formation of both 2,3-dibromoalkene products (6 ppm, 4.64 ppm) in addition to elimination side reactions as a result of thermal activation (6.4 – 5.6 ppm).

559 kDa 80 % *cis-gBC*C-PB



b]

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) after thermolysis (165 °C, methyl benzoate, N_2, 17 hours) of *gBC*C polymer shows preferential ring opening of the *cis-syn*-Cl isomer of *cisgBC*C-PB (4.65 ppm) as a result of thermal activation.

Compression Testing

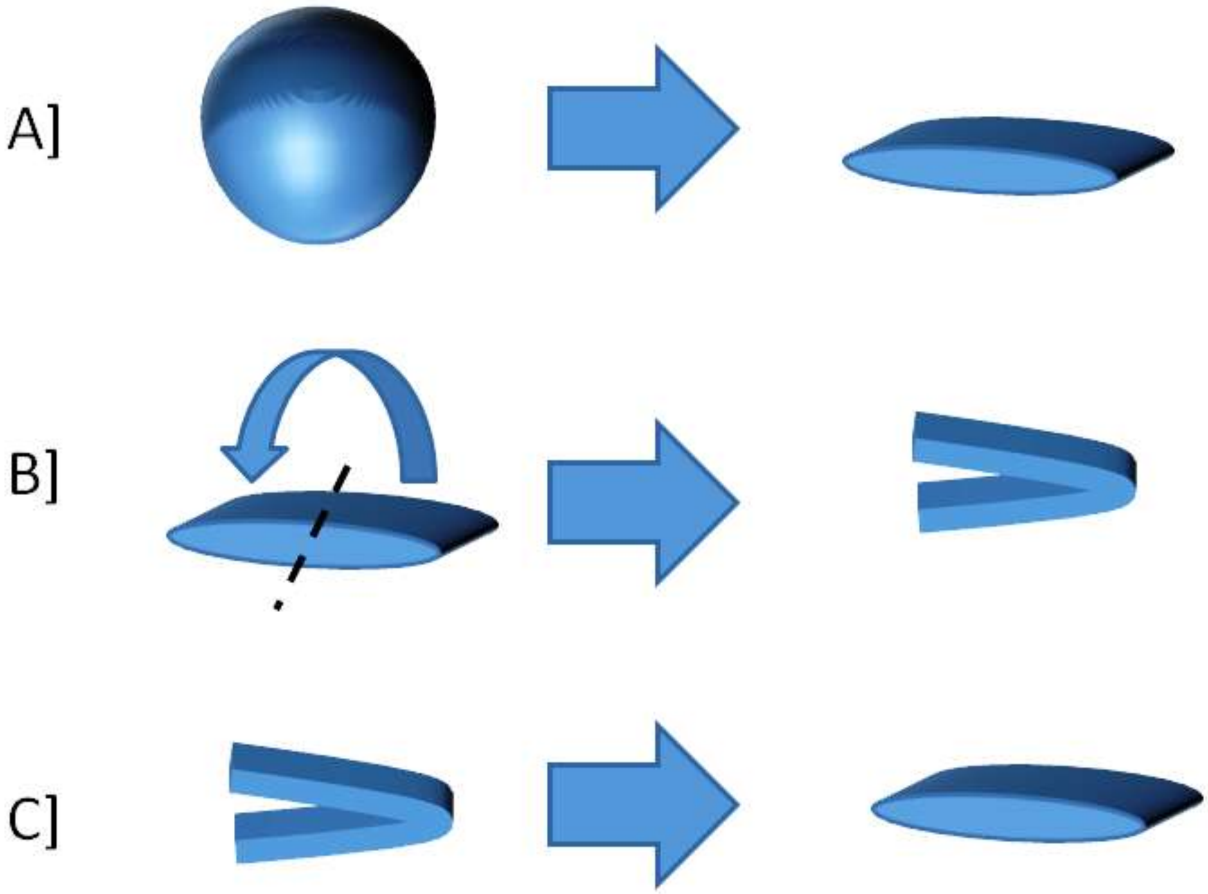


Figure S25. Schematic describing the procedure for solid state activation of *g*DHC-PB polymers. First, [A] the polymer (70-80 mg) is placed in the KBr pellet press and compressed at a given pressure and amount of time. After the allotted number of compressions, the polymer is removed, folded in half [B] and subjected to a second round of compressions [C]. The polymer is removed, refolded ([C]→[B]→[C]) and subjected to additional compressions.

411 kDa 98 % *cis*-*g*DCC-PB

Time Dependence

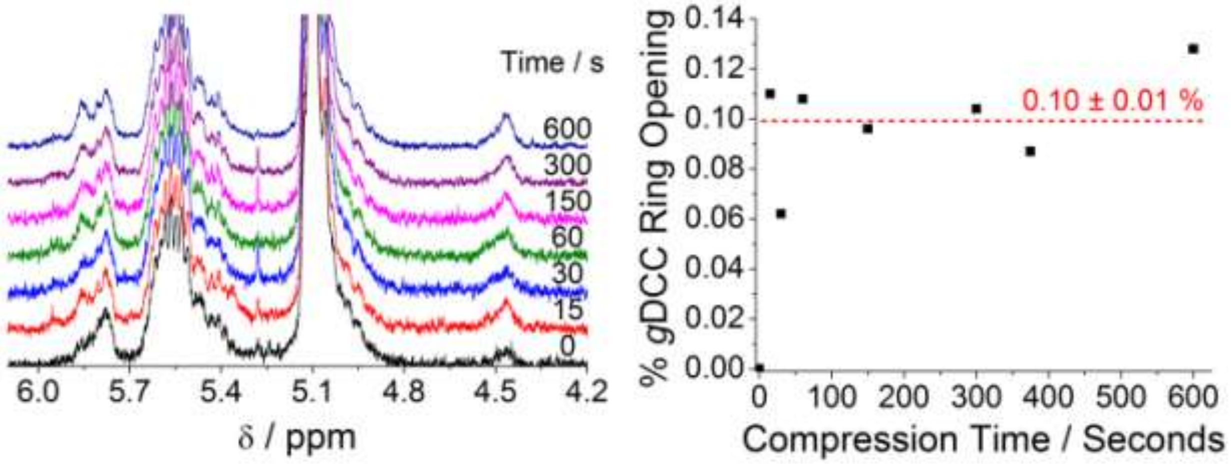


Figure S26. The amount of *g*DCC ring opening is independent of the amount of time the polymer is held under constant compression (178 MPa, 25 °C). Ring opening was monitored by ^{1}H NMR (left, 500 MHz, $CDCl_3$) and the subsequent ring opening was plotted versus the compression time (right) resulting in an average of 0.10 ± 0.01 % opening for all compressions. Time point at 375 seconds taken from compression (6.25 minutes, 178 MPa, 25 °C) of *g*DCC polymer **A**.

Flip Dependence

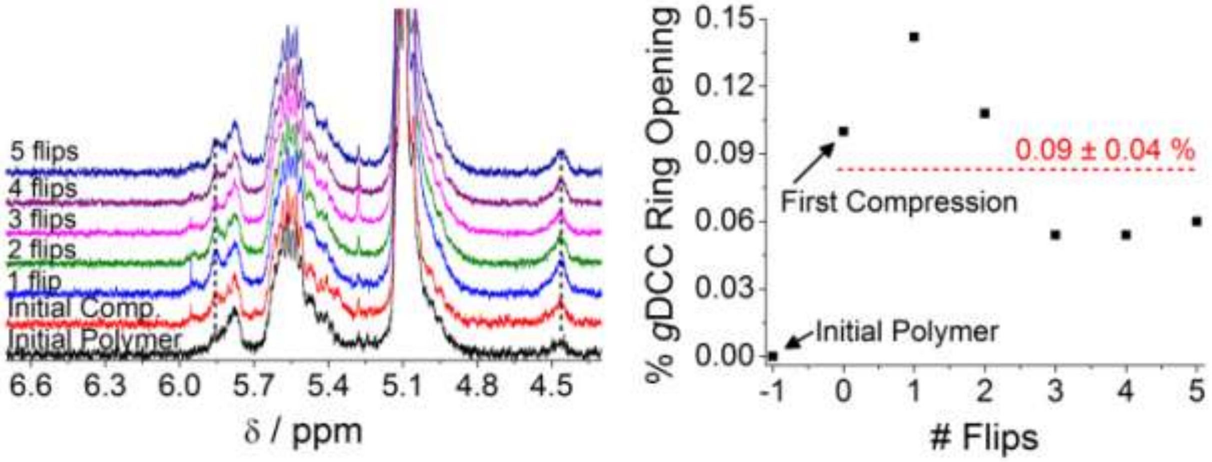
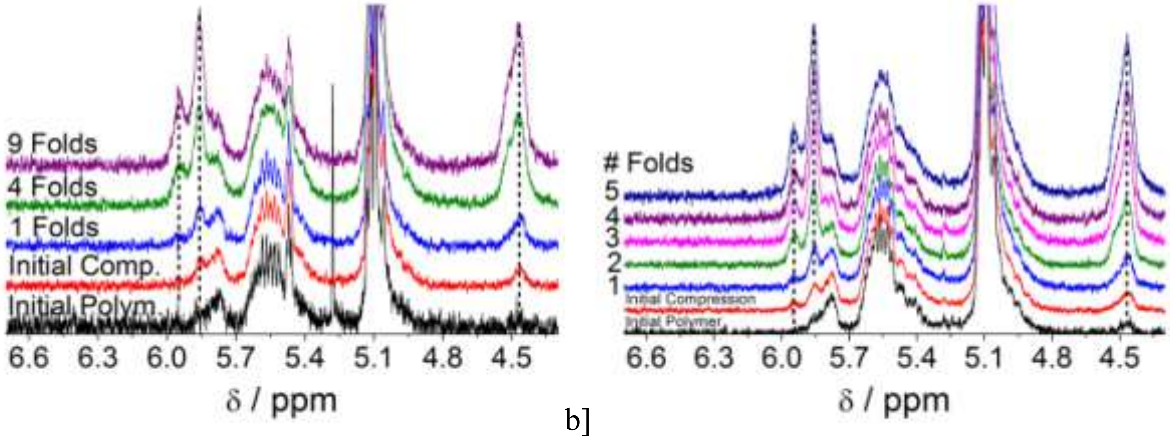


Figure S27. The amount of *g*DCC ring opening is independent of flipping the polymer 180° in between a 5-compression set (178 MPa, 15 s on / 3 s off). Ring opening was monitored by ^{1}H NMR (left, 500 MHz, $CDCl_3$) and the subsequent ring opening was plotted versus the number of times the polymer was flipped (right) between 5-compression sets (15 s on / 3 s off).

Fold Dependence



a] b]

Figure S28. The amount of *g*DCC ring opening is dependent on the number of times the polymer is folded between 5-compression sets (15s on / 3s off; 178 MPa). Ring opening as monitored by ^{1}H NMR (500 MHz, $CDCl_3$) during compression of *g*DCC polymer **A** [a] and **B** [b].

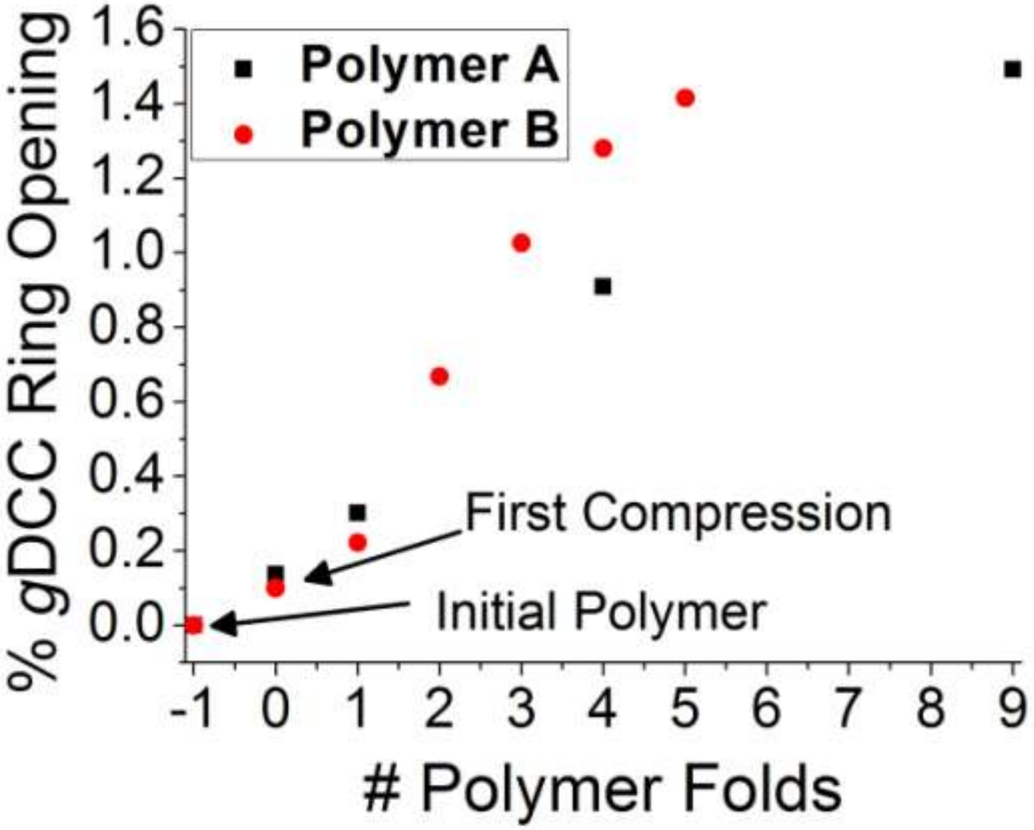


Figure S29. Plot of the percent *g*DCC ring opening during compression testing of *g*DCC polymers **A** and **B** (178 MPa, 5-compression sets followed by folding the polymer in half and subsequent 5-compression sets (15s on / 3 s off).

Compression Set Dependence

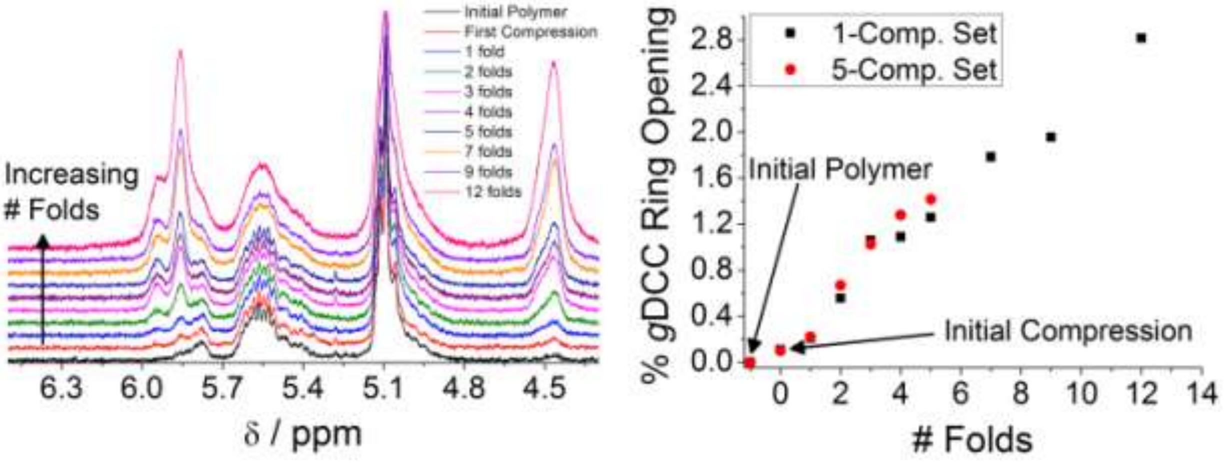


Figure S30. The activation of *g*DCCs does not depend on the application of a 5-compression set. This data was collected during compressive ring opening (178 MPa) of *g*DCC polymer. The sample was folded after each 15 s compression after which the ring opening was monitored by ^{1}H NMR (left). The activation profile versus the number of times the polymer was folded in half (right) matches data obtained when folding the polymer between 5-compression sets of 15s on / 3 s off.

Ring Opening per Polymer Fold

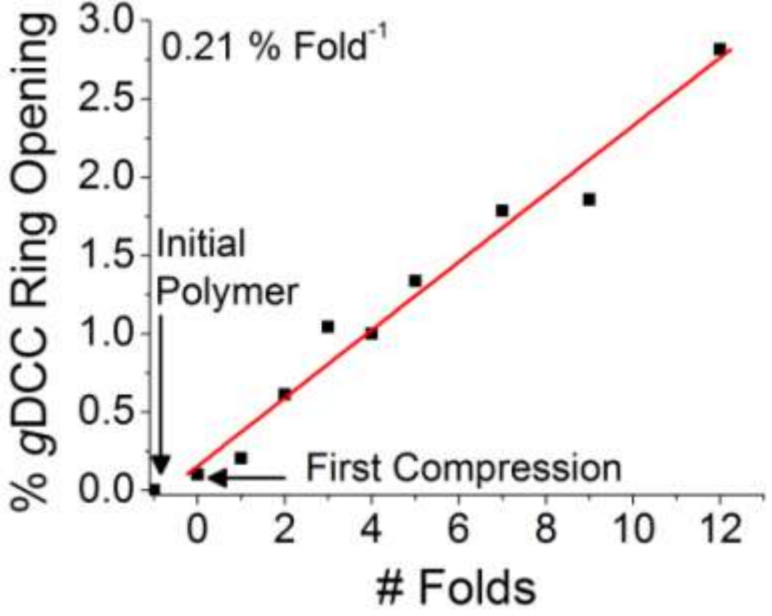


Figure S31. Linear regression fitting of compressively activated *g*DCC polymer (average data points from compressions of polymer A, polymer B, 178 MPa and at different compression sets) results in 0.21 % ring opening per polymer Fold.

Applied Pressure Dependence

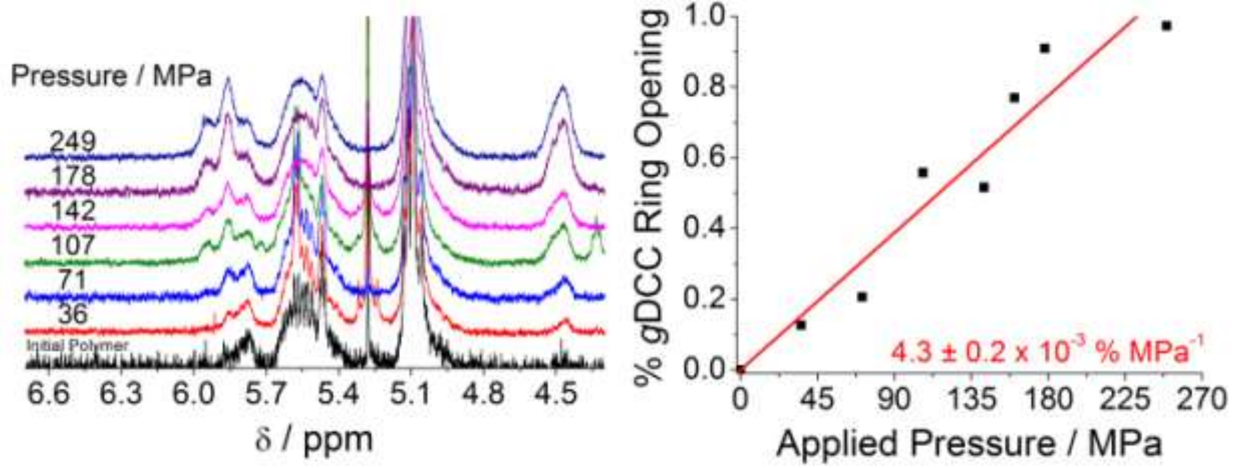


Figure S32. The ring opening of *g*DCC (polymer **A**) in the solid state is linear versus the applied pressure. (Left) ^{1}H NMR (500 MHz, $CDCl_3$,) shows that increasing the applied pressure during *g*DCC-PB compressions leads to a linear increase in the percent of ring opening (right). In each experiment, the polymer was compressed 25 times (15 seconds on/3 seconds off); 5 compressions set, and the polymer was removed for a refold every 5 compressions.

Lorentzian Curve Fitting (1): Constant Pressure

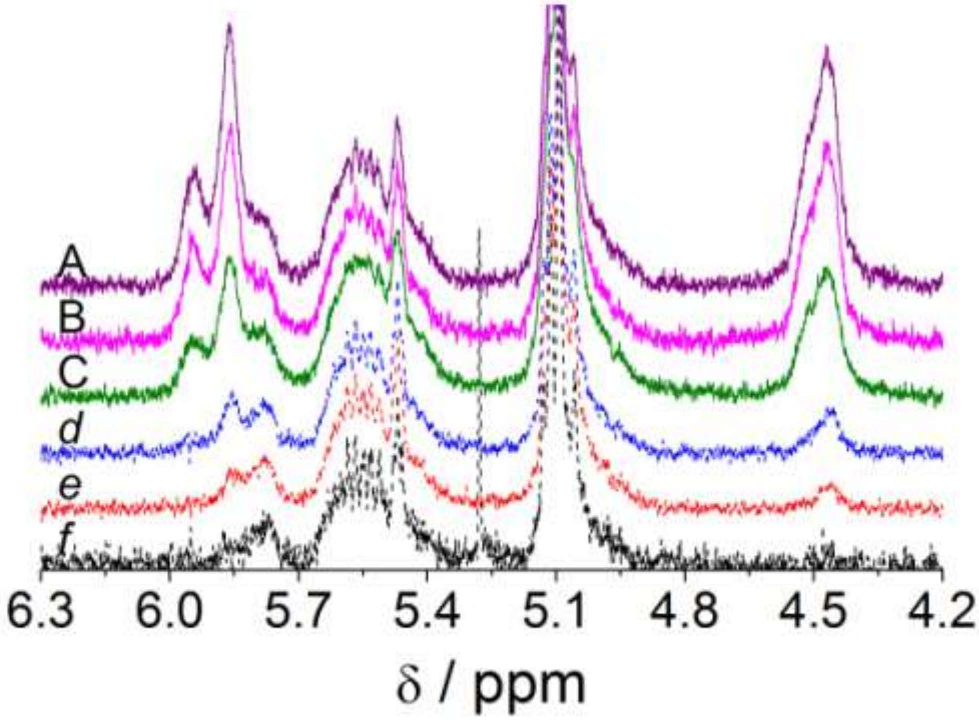


Figure S33. ^{1}H NMR spectra after *g*DCC polymer (**A**) compression to **178 MPa** to varying numbers of compressions. [A] 10 compressions, 15 seconds each. After each compression the polymer was removed, folded and subjected to compression; 10 compressions, 10 polymer folds. [B] 50 compressions, 15 seconds each. After 5 compressions (15 s on / 15 s off) the polymer was removed, folded and resubjected to a 5-compression set; 50 compressions; 10 polymer folds. [C] 25 compressions, 15 seconds each. After 5 compressions (15 s on / 15 s off) the polymer was removed, folded and resubjected to a 5-compression set; 25 compressions; 5 polymer folds. [d] 10 compressions, 15 seconds each. After 5 compressions (15 s on / 15 s off) the polymer was removed, folded and resubjected to a 5-compression set; 10 compressions; 2 polymer folds. [e] 5 compressions, 15 seconds each. After 5 compressions (15 s on / 15 s off) the polymer was removed for NMR analysis. [f] initial polymer spectrum. Due to the low signal to noise ratio in *d* and *e*, Lorentzian curve fitting was completed for A, B and C only.

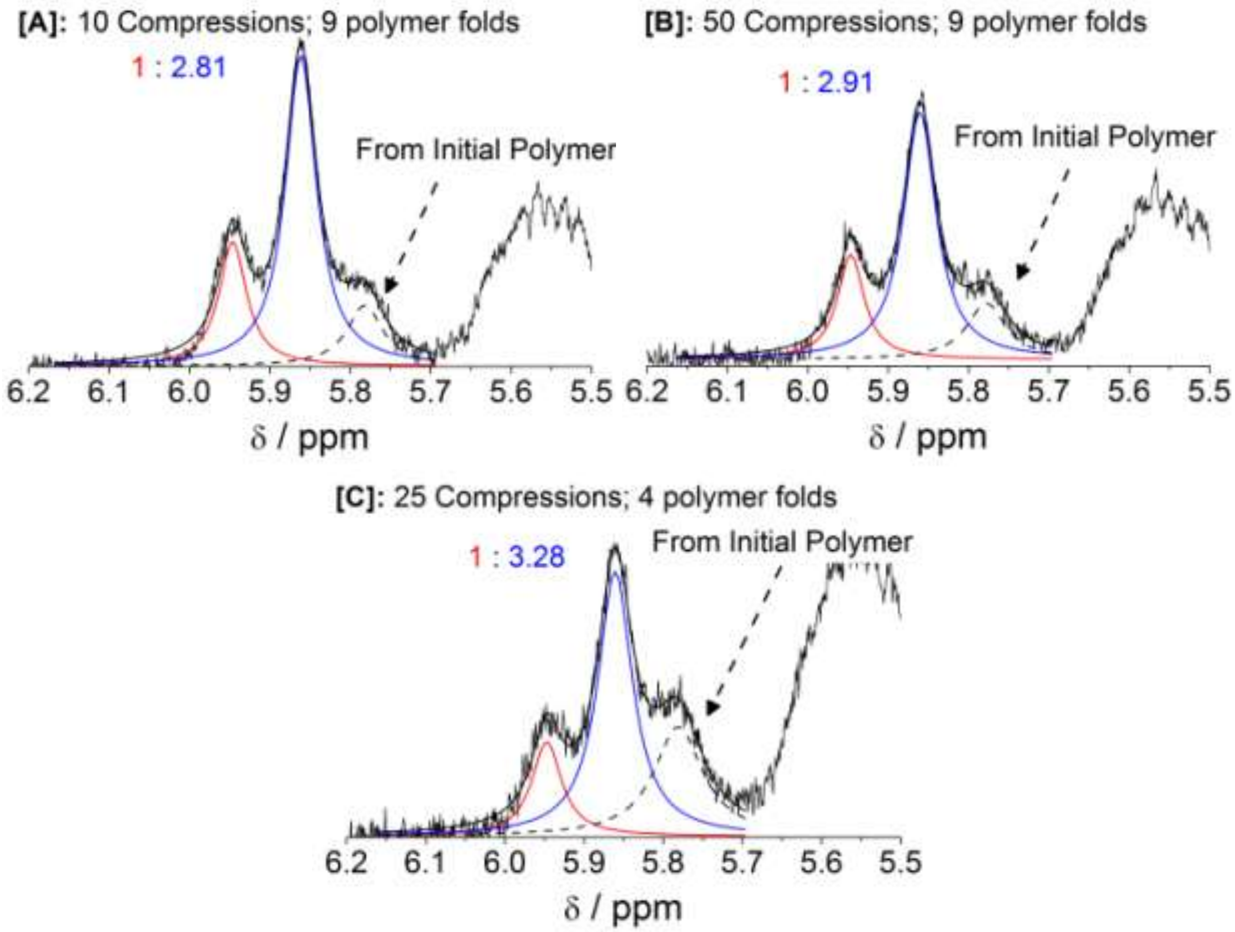


Figure S34. Lorentzian curve fits for compressed samples (178 MPa) of varying numbers of compressions and polymer folds.

Lorentzian Curve Fitting (2): Constant Compression Set

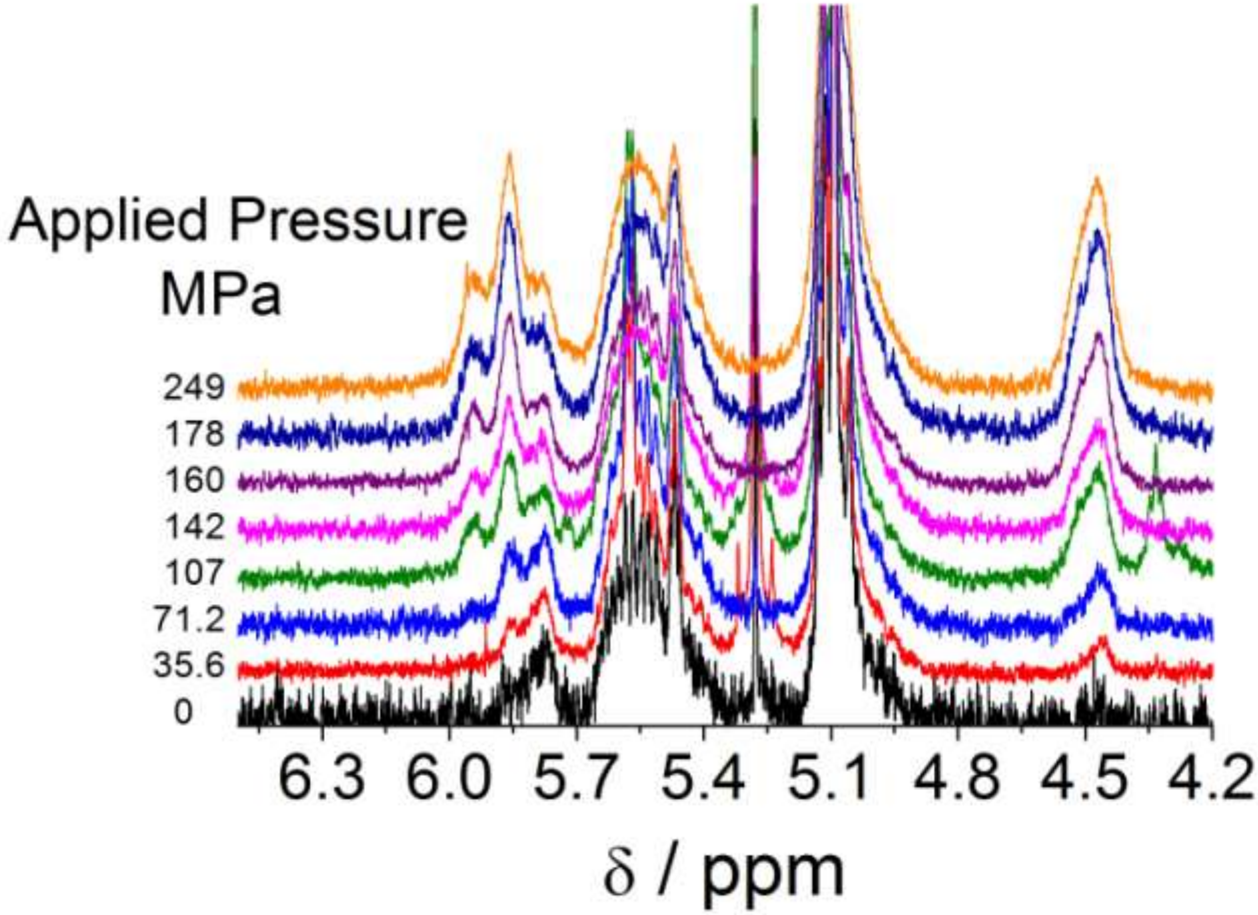


Figure S35. ^{1}H NMR spectra (500 MHz, $CDCl_3$; CH_2Cl_2 impurity observed at 5.25 ppm) after *cis*-*g*DCC polymer **(A)** was compressed to different stresses. In all cases the polymer was subjected to 25 compressions at 15 s on / 3 s off. The polymer was removed from the press after each 5 compressions and refolded before further compressions; 25 compressions, 4 polymer folds. Due to low signal to noise ratios, fits were performed for applied pressures above 100 MPa.

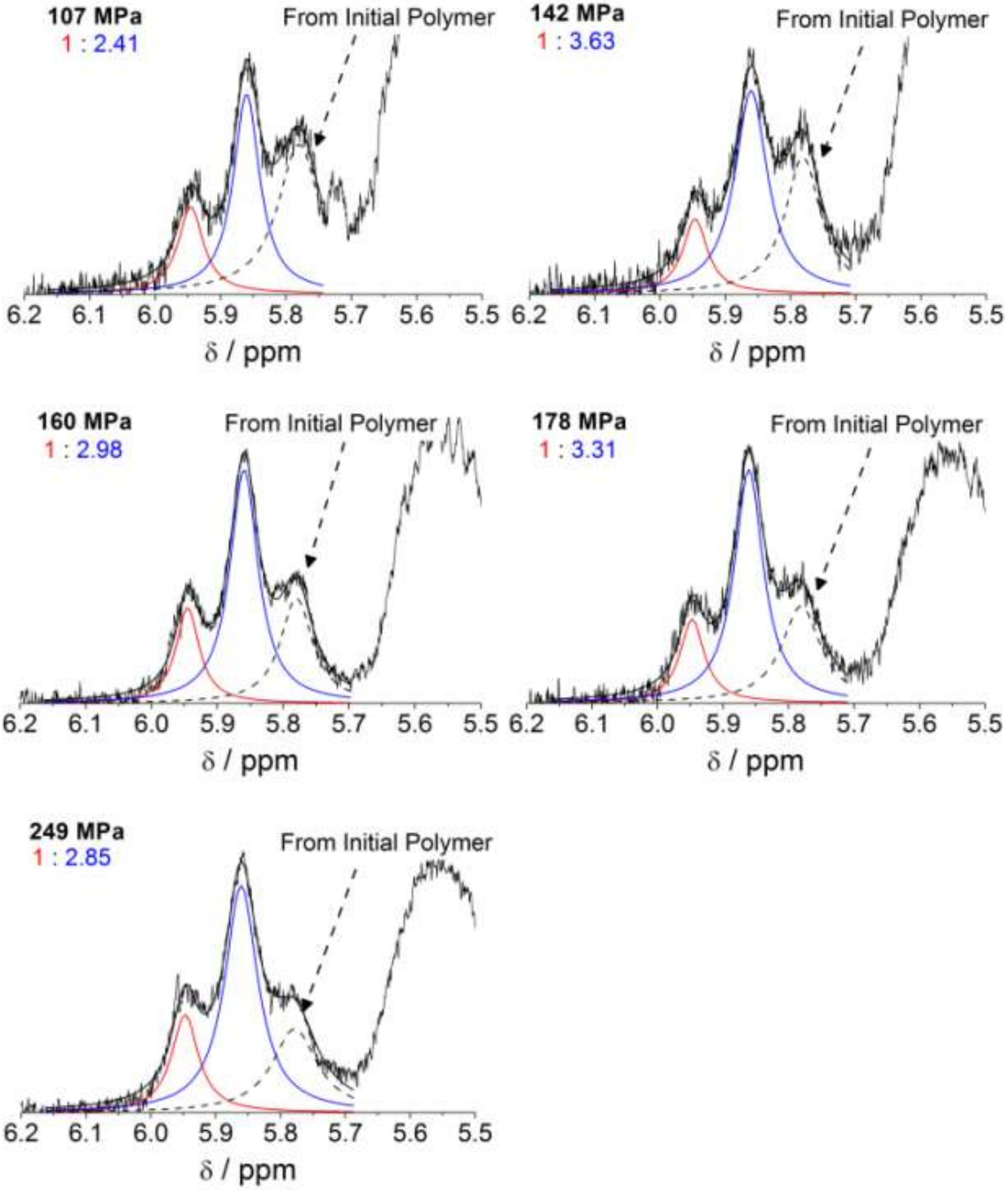


Figure S36. ^{1}H NMR Lorentzian curve fitting analysis for compressed samples at different pressures. The resulting average distribution of proton resonances at 5.96 : 5.85 ppm = 1 : 3.02 for all samples subjected to Lorentzian curve fitting analysis.

285 kDa 87 % *cis*-*g*DBC-PB

Fold Dependence

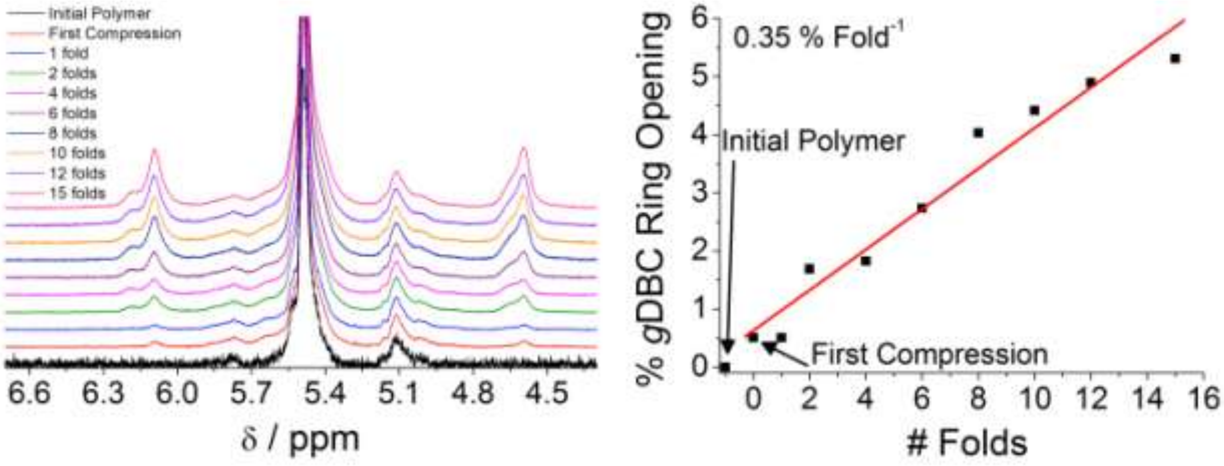


Figure S37. Ring opening of *g*DBC was monitored by ^{1}H NMR (left, 500 MHz, $CDCl_3$) as a function of the number of times the polymer is folded in half during compressive activation (178 MPa). The polymer was refolded after each 15 s of compression at 178 MPa.

Pressure Dependence

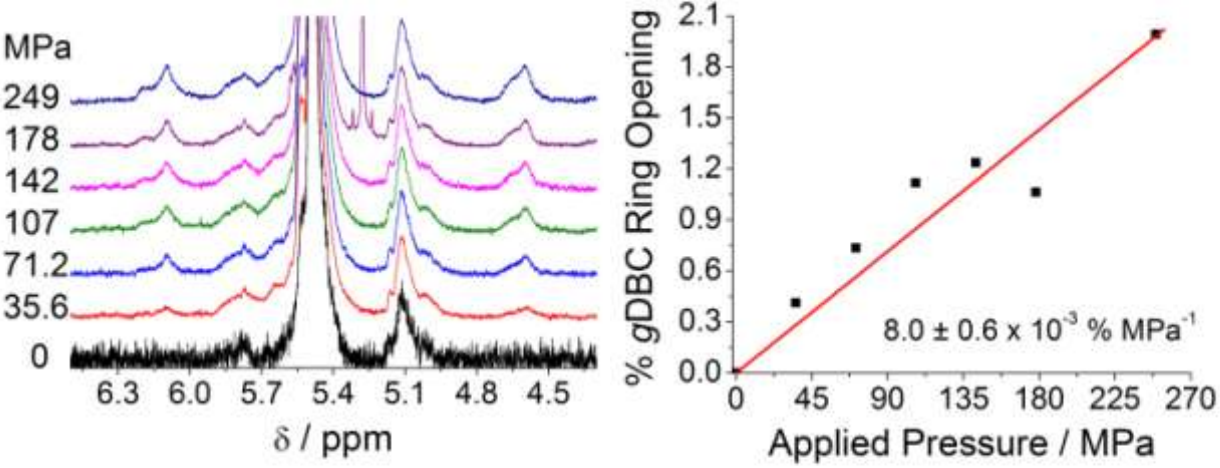


Figure S38. The ring opening of *g*DBC in the solid state is linear versus the applied pressure. (Left) ^{1}H NMR (500 MHz, $CDCl_3$) shows that increasing the applied pressure during *g*DBC-PB compressions leads to a linear increase in the percent of ring opening (right). In each experiment, the polymer was compressed 25 times (15 seconds on/3 seconds off) and the polymer was removed for refold every 5 compressions (4 folds total).

559 kDa 80 % *cis*-*g*BCC-PB

Compression Dependence

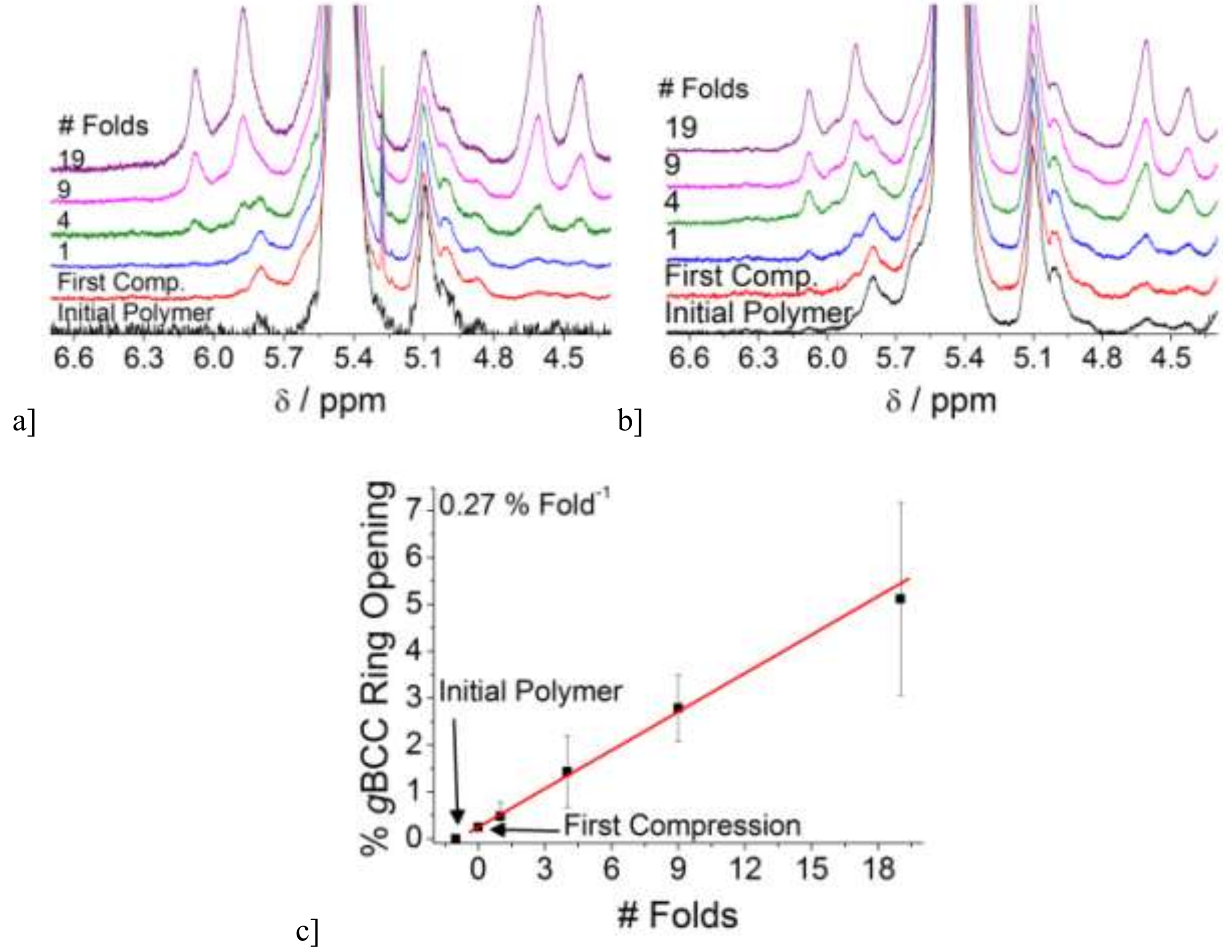


Figure S39. Ring opening of *gB*CC was monitored by ^{1}H NMR (left, 500 MHz, CDCl$_3$) as a function of the number of compressions on solid polymer (70-80 mg) on different days [a, b]. Compression data from [a] was conducted on polymer directly from dried polymer after workup of the polymer. Compression data from [b] was collected on polymer that was reprecipitated and dried prior to use; the reason that the initial ^{1}H NMR spectra area inequivalent, though the extent of *g*BCC mechanophore contents are the same. Compressions were performed in 5-compression increments. The polymer was placed on the KBr press and subjected to five compressions (178 MPa), holding each compression at 178 MPa for 15 seconds followed by a 3 second pressure release. After every five compressions, the polymer sample was removed from the press, folded in half and subjected to another five compressions (15 seconds on, 3 seconds off). A plot of the amount of ring opening versus the number of times the polymer was ‘folded’ is linear with a slope of 0.27 % ring opening per Fold. Error bars indicate the standard deviation of the data point between data points sets.

Pressure Dependence

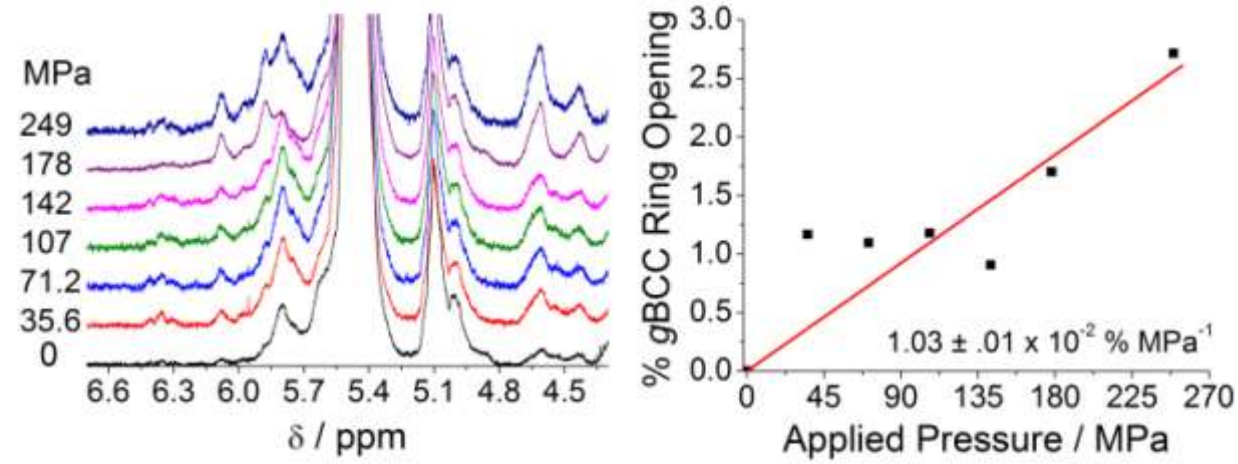


Figure S40. The ring opening of *gBC*C in the solid state is ~linear versus the applied pressure. (Left) ^{1}H NMR (500 MHz, $CDCl_3$) shows that increasing the applied pressure during *g*BCC-PB compressions leads to a linear increase in the percent of ring opening (right). In each experiment, the polymer was compressed 25 times (15 seconds on/3 seconds off), a total of 5 compression sets with 4 polymer Folds.

Tensile Testing

Sample Preparation

4 g g-DBC-linked polymer was dissolved in 40 mL chloroform. The resulting solution was poured into a 40 mm x 80 mm rectangular Teflon mold. Chloroform was evaporated off under room conditions for 24 hours, and further dried for 1 hr under vacuum. The resulting polymer had a thickness of 0.40 mm. Rectangular samples were cut from the bulk polymer for tensile testing. The polymer was stored at 3 °C to inhibit thermal activation and brought to room temperature before testing.

Tensile Testing

Samples were initially tested using a custom built load frame at room temperature (22 °C). Monotonic tensile tests were run at a strain rate of 0.1 s^{-1}. Failure occurred at a stretch ratio of up to 22, where stretch ratio is defined as gauge length during testing divided by undeformed length. Additional samples were prestretched and held for 600 s at a stretch ratio of 8, in an effort to align polymer chains in the direction of force, and the load was removed. These plastically deformed samples were then retested in tension, with a higher stress at failure. Samples were dissolved in $CDCl_3$ after failure and NMR spectra were taken. ^{1}H-NMR spectrum failed to indicate any activity of the mechanophore under either testing condition.

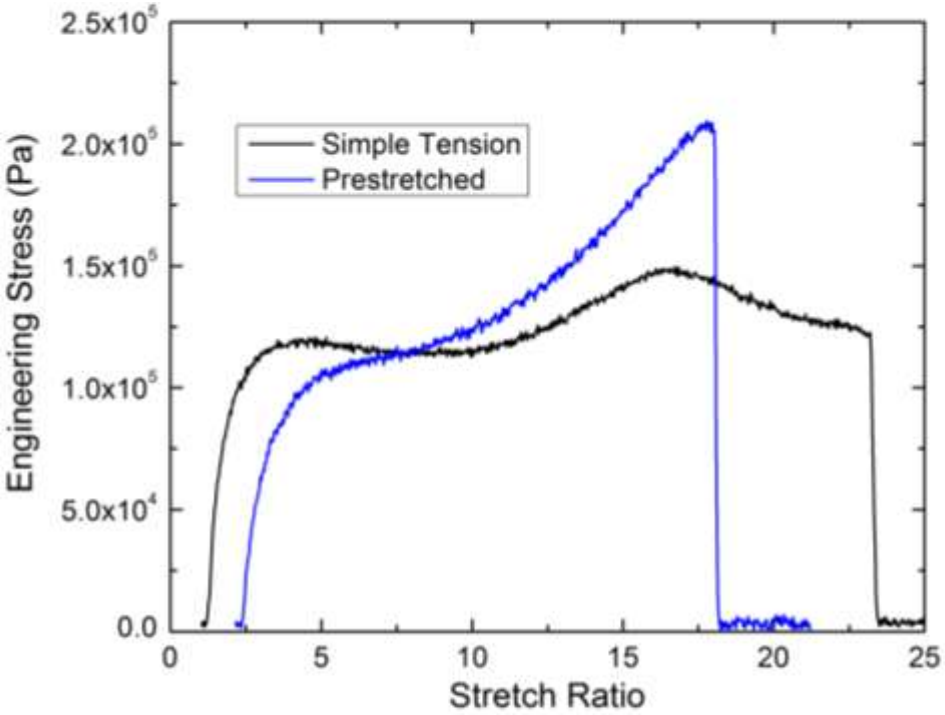


Figure S41. Loading curves for *g*DBC polymer samples tested in tension at room temperature (22 °C). The prestretched sample was plastically deformed to align mechanophores in the draw direction prior to testing.

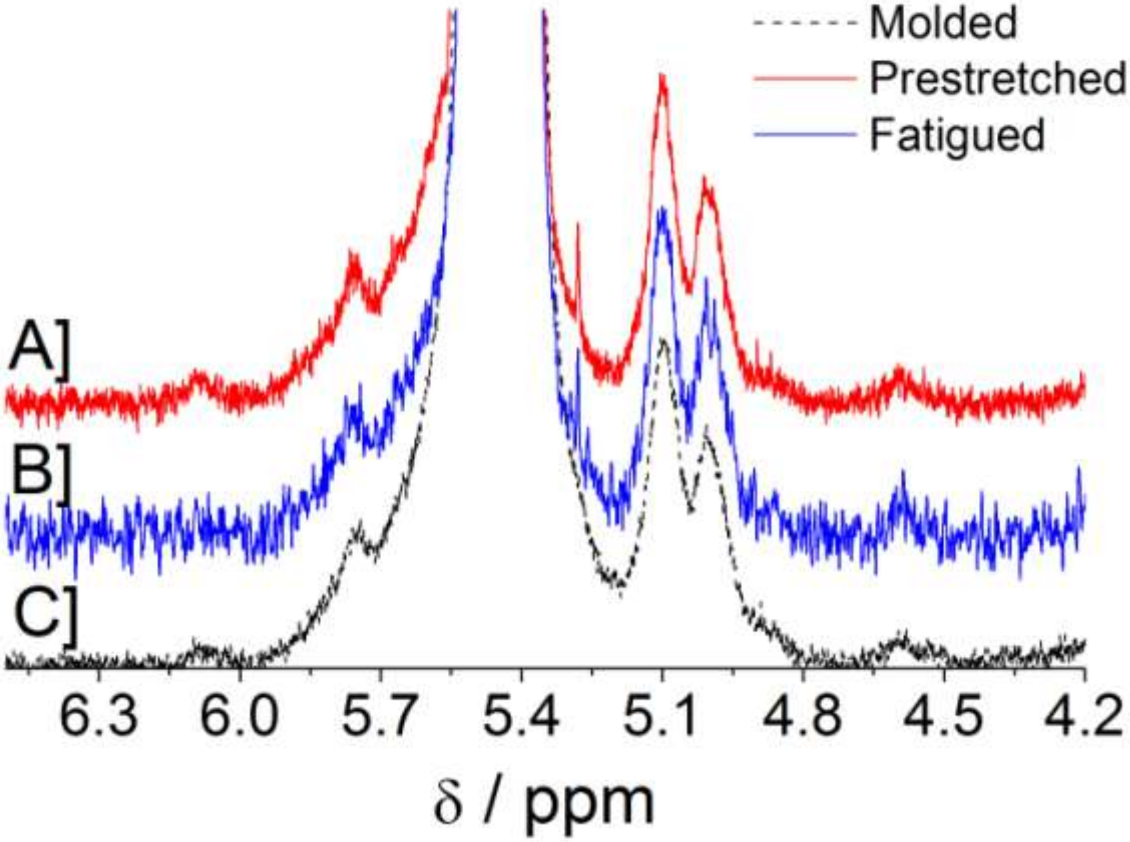


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of 66 % *cis*-*g*DBC polymer subjected to tensile fatigue at room temperature. A] a polymer sample prestretched then stretched to failure. B] A polymer sample directly tested to failure and C] NMR of the initial polymer.

Temperature Control

Dynamic mechanical analysis equipment (TA Model RSA3) was used to control the temperature of the polymer for additional testing. The glass transition temperature for this polymer was determined to be approximately -10°C from the tan(delta) peak of modulus vs. temperature curves. Samples were then tested at a range of temperatures near and below Tg, in order to impart higher force to the polymer and across the mechanophore. Loading curves for these temperature ranges can be seen in Fig S43. Substantially higher stresses were applied, but again no activation was apparent via NMR.

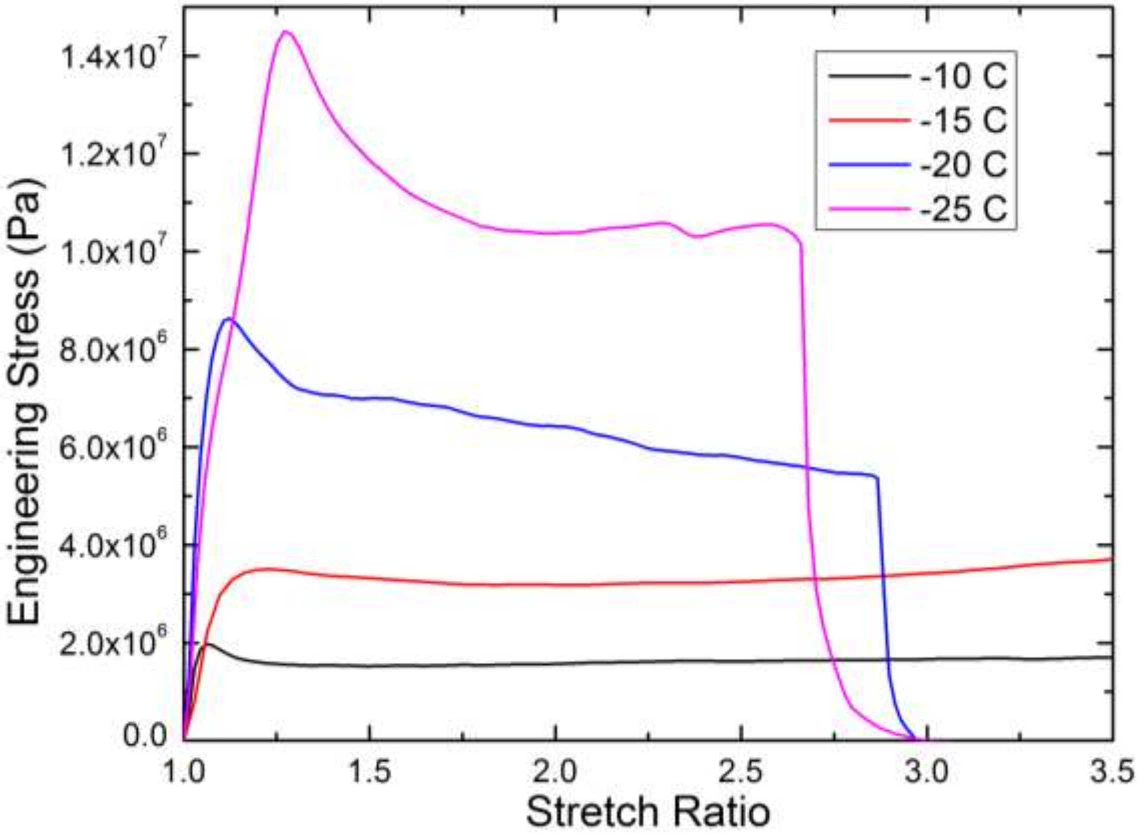


Figure S43. Loading curves for *g*DBC polymer tested at a range of temperatures below T_g.

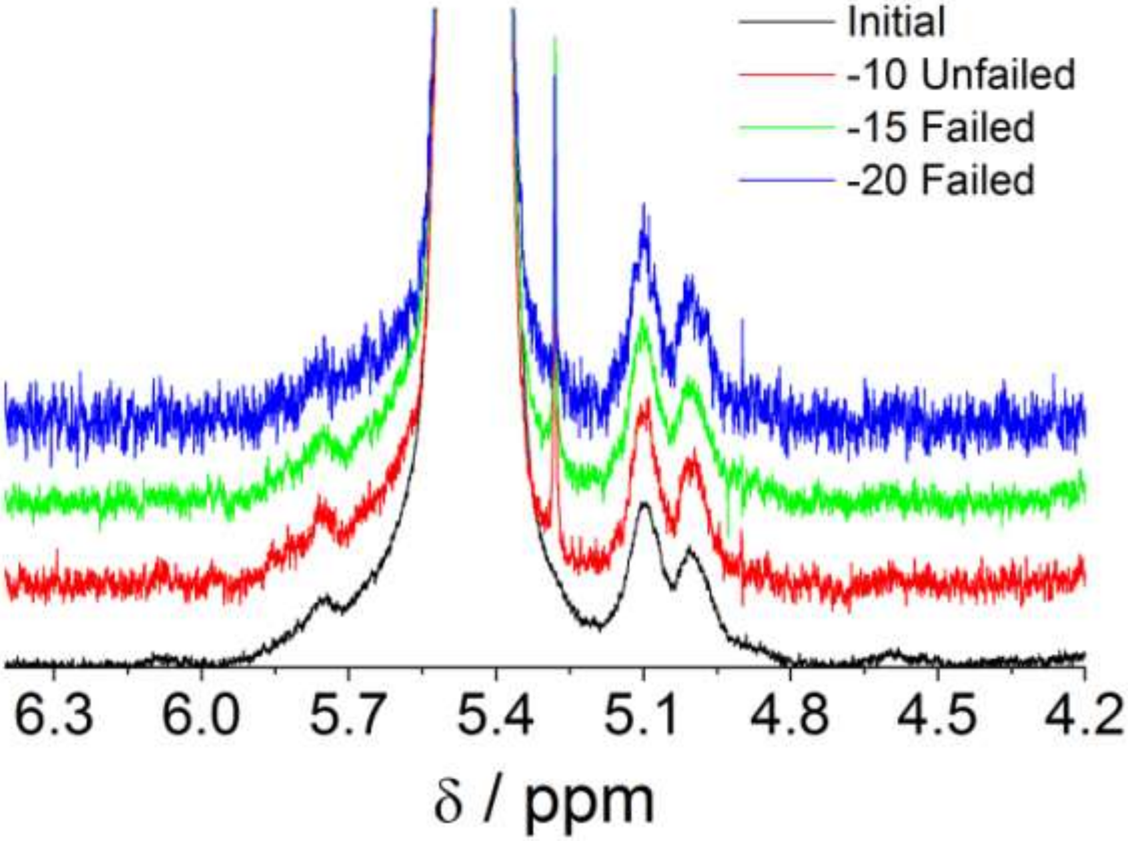


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectra taken after tensile testing of 66 % *cis*-*g*DBC-PB. A polymer sample was subjected to tensile deformation at -10 °C (red) and a sample was removed before the film failed. Two additional polymer films were subjected to tensile deformation at both -15 °C (green) and -20 °C (blue) until failure. In all cases *g*DBC ring opening to 2,3-dibromoalkene is not observed.