Supporting Information For:

Mechanochemically Triggered Bond Formation in Solid-State Polymers

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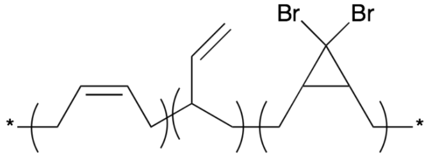
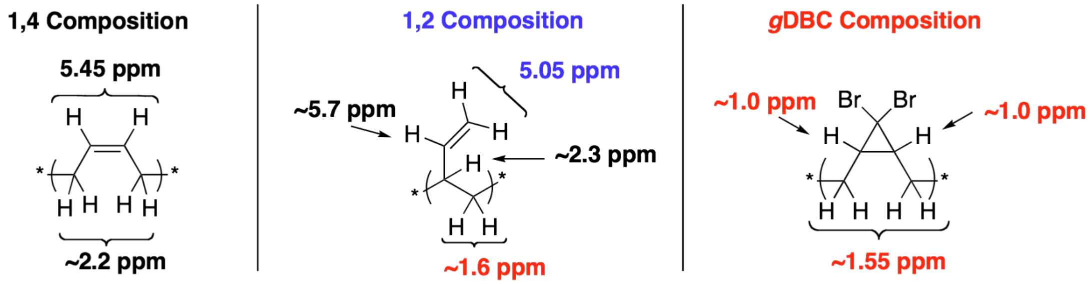
General Calculations

Calculating Percent Functionalization of *g*DBC-PB from ^{1}H-NMR





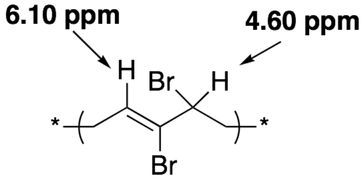
All chemical shifts were referenced to the residual $CHCl_3$ peak at 7.24 ppm and 77.23 ppm for ^{1}H- and ^{13}C-NMR, respectively. Percent functionalization is calculated from the relative integrations in the ^{1}H-NMR spectra as follows. The peak at 5.45 ppm represents the 2 vinyl protons of 1,4-polybutadiene and therefore the peak areas are referenced to that peak in the ^{1}H NMR. There is overlap between the peaks at ~5.7 ppm and ~2.3 ppm from two protons on the 1,2-polybutadiene monomers and the resonances associated with the 1,4-polybutadiene, and therefore the area of the peak at 5.05 ppm (representing 2 protons) is subtracted from the sum of the area of the 5.45 ppm resonance and 2.2 ppm resonance to get the total area attributed to the six protons on the 1,4-polybutadiene monomers. The only peak that represents solely 1,2-polybutadiene is that at 5.05 ppm, which is attributed to 2 protons. Finally, the resonances from the *g*DBC monomers occur in a broad peak at 1.0 - 1.6 ppm. Because two protons from the 1,2-polybutadiene also show up in this region, the area of the peak at 5.05 ppm (2H) is subtracted to give the area due to the 6 protons from the *g*DBC. Normalizing to the number of protons in each monomer gives:

(1,4) Composition: (5.45 ppm area – 5.05 ppm area + 2.2 ppm area) / 6 = **A**
(1,2) Composition: (5.05 ppm area) / 2 = **B**
(*g*DBC) Composition: (1.58 ppm area – 5.05 ppm area) / 6 = **C**

Percent Functionalization = C / (A + B + C) * 100 %

Similar analyses are used for calculating percent functionalization of *g*DCC-PB and *g*BCC-PB. Note: Peak deconvolution is not used to determine peak integrations due to complications that would arise from polymer microstructure.

Calculating Percent Ring-Opening of *g*DBC-PB from ^{1}H-NMR



The percent ring-opening is calculated by determining an "equivalent" of ring-opened protons. The two protons indicative of ring-opening appear at 6.10 ppm and 4.60 ppm for *g*DBC. By averaging the area of these peaks and then comparing that to the "equivalent" of mechanophore from the previous page "**C**", the percent ring-opening is determined.

[(6.10 ppm area + 4.60 ppm area) / 2] / C * 100 %

Respective peak resonances are used for calculating percent ring-opening of *g*DCC-PB and *g*BCC-PB.

Calculating Molecular Weight from GPC

Gel permeation chromatography analyses were performed with a Varian Prostar Model 210 pump, a Varian Prostar Model 320 UV/Vis detector set to 254 nm detection, a Wyatt Dawn EOS multi-angle light scatterer (MALS), Wyatt QELS (quasi-electric light scattering), Wyatt Optilab DSP Interferometric Refractometer (RI), and a Agilent Technology PL gel column (7.5 X 300 mm, 79911GP-504 (10^4 Å)) in tetrahydrofuran at 22°C (room temp.). Molecular weights were calculated by multi-angle light scattering (MALS) gel permeation chromatography (GPC) using ASTRA V Version 5.3.4.16. Refractive index increment (dn dc^{-1}) values were measured directly using the RI detector.

Probability of Reacting Calculations

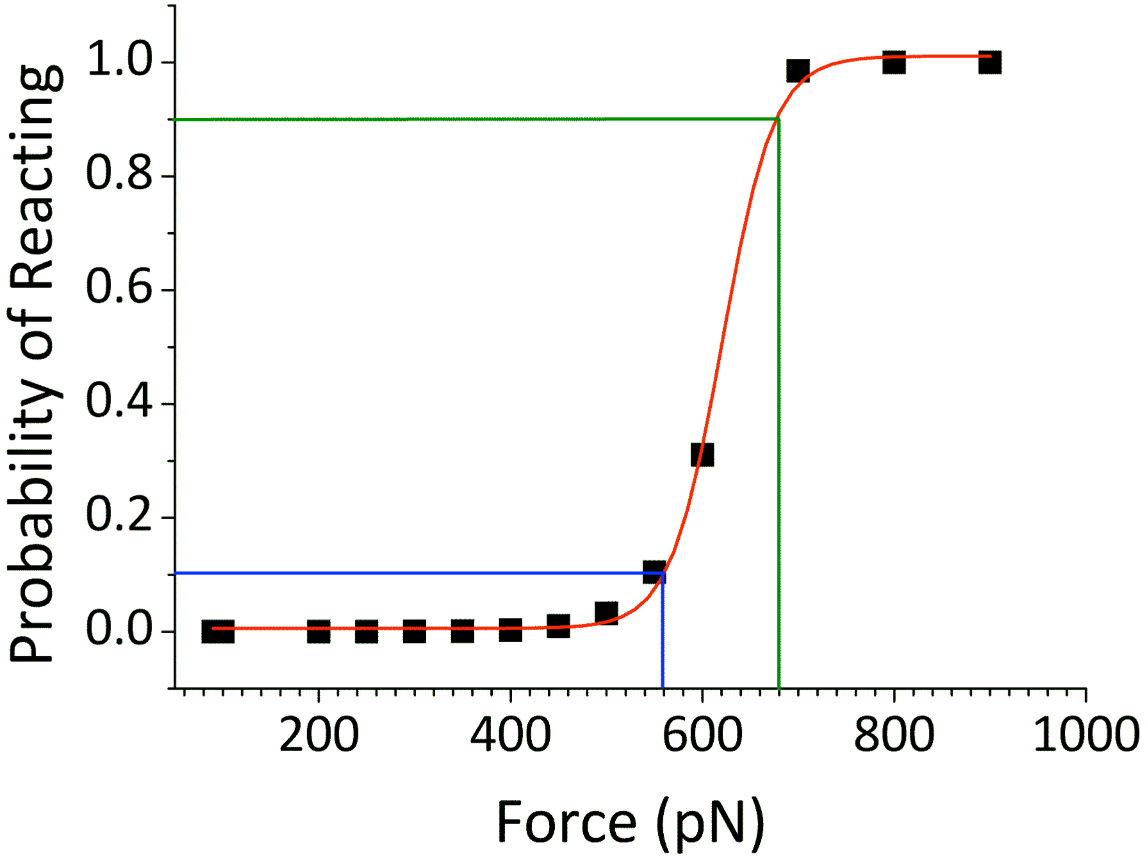


Figure S1. Relationship between applied force and probability of mechanophore ring-opening occurring over a period of 600 seconds at that force, assuming the rate vs. force relationship in the main text and reference 8.

Probability of reacting = 1 – exp ^ (-k_F * t)
Where $k_F = k_o$ exp ^ [($\Delta x^{\ddagger}$ * F)/(k_B*T)]
Where $k_o = 2.868\text{x}10^{-10}$
$\Delta x^{\ddagger}$ = 1.05 x 10^{-10} m
F = Force
K_B = Boltzmann’s constant
t = 600 seconds
T = 313 K

Polymer Synthesis and Characterization

4.9x10^5 Da 67 % *gem*-dibromocylcopropanated polybutadiene (*g*DBC-PB)

12.04 g (0.223 moles) *cis*-PB, 8.127 g (.0223 moles) CTAB and 86.54 mL (.989 moles) CHBr$_3$ were dissolved in 500 mL CH$_2$Cl$_2$ and deoxygenated with bubbling N$_2$ for 30 minutes. To a separate round-bottomed flask was dissolved 44.6 g (1.12 moles) NaOH in 100 mL DI-H$_2$O and the solution was deoxygenated with bubbling N$_2$ for 30 minutes. After 30 minutes, the NaOH solution as added dropwise to the PB solution and the reaction was allowed to proceed for 18 hours under a headspace of N$_2$. After 18 hours the solution was washed 3X with DI-H$_2$O, rotovapped to minimal volume and the polymer was precipitated with methanol. The polymer was reprecipitated twice more from CH$_2$Cl$_2$ with methanol and dried overnight on high vacuum. ^{1}H NMR (400 MHz, CDCl$_3$) d 5.45 (b, 2.0H), 5.05 (b, 0.12H), 2.21 (m, 4.2H), 1.58 (b, 13.4H), Trace CH$_2$Cl$_2$ at 5.281 ppm and trace CH$_3$OH at 3.479 ppm. Copolymer composition = 30 % 1,4-PB, 2.9 % 1,2-PB, 67 % *g*DBC. Theoretical molecular weight calculated as follows: 1.6x10^5 Da PB starting material contains 2884 monomer units. Upon functionalization, the per monomer contribution to the polymer molecular weight increases from 54.09 Da to 225.91 Da (*g*DBC). For a functionalization of 67 %, then the final molecular weight is: Molecular Weight = (0.67 * 2884 * 225.91) + (0.33 * 2884 * 54.09) = 4.9x10^5 Da

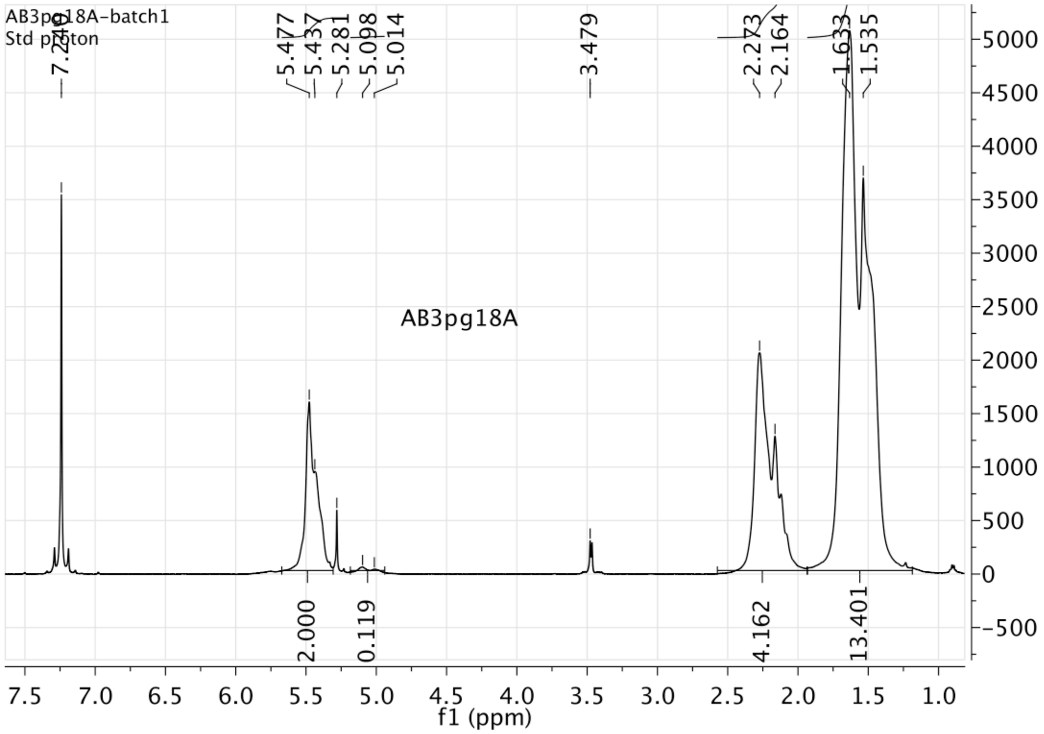


Figure S2. ^{1}H-NMR of 4.9x10^5 Da, 67 % *g*DBC-PB.

8.6x10^5 Da 79 % *gem*-dibromocylcopropanated polybutadiene (*g*DBC-PB)

19.91 g (0.3681 moles) *cis*-PB, 13.484 g (.0367 moles) CTAB and 161 mL (1.841 moles) $CHBr_3$ were dissolved in 2 L CH_2Cl_2 and deoxygenated with bubbling N_2 for 1 hour. To a separate round-bottomed flask was dissolved 75.25 g (1.881 moles) NaOH in 200 mL DI-H_2O and the solution was deoxygenated with bubbling N_2 for 30 minutes. After 30 minutes, the NaOH solution as added dropwise to the PB solution and the reaction was allowed to proceed for 18 hours under a headspace of N_2. After 18 hours the solution was washed 3X with DI-H_2O, rotovapped to minimal volume and the polymer was precipitated with methanol. The polymer was reprecipitated twice more from CH_2Cl_2 with methanol and dried overnight on high vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) d 5.49 (b, 2.00H), 5.05 (b, 0.17H), 2.22 (m, 4.1H), 1.58 (b, 24.1H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.8, 77.23, 36.762, 33.75, 33.498, 27.489, 26.517, 26.43, 26.262, 26.198. Trace CH_2Cl_2 and CH_3OH present at 53.651 and 51.123 ppm, respectively. Copolymer composition = 19 % 1,4-PB, 2 % 1,2-PB, 79 % *g*DBC. Molecular weight calculated by GPC as described on page S4, dn/dc = 0.095 mL/g

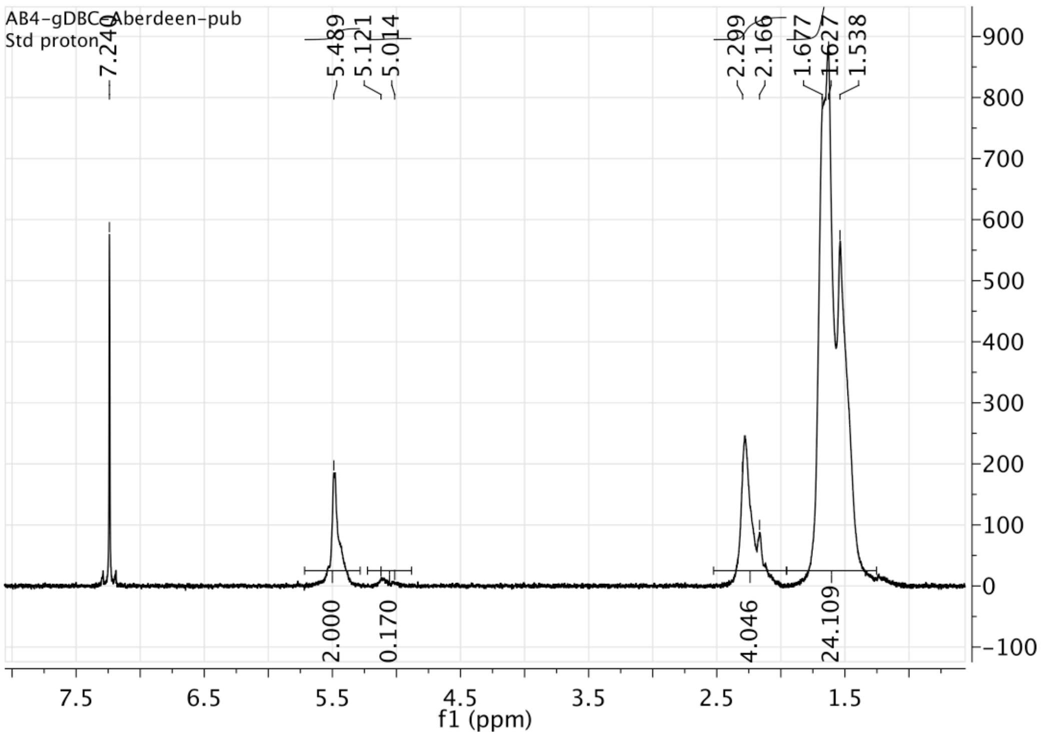


Figure S3. ^{1}H-NMR of 8.6x10^5 Da, 79 % *g*DBC-PB.

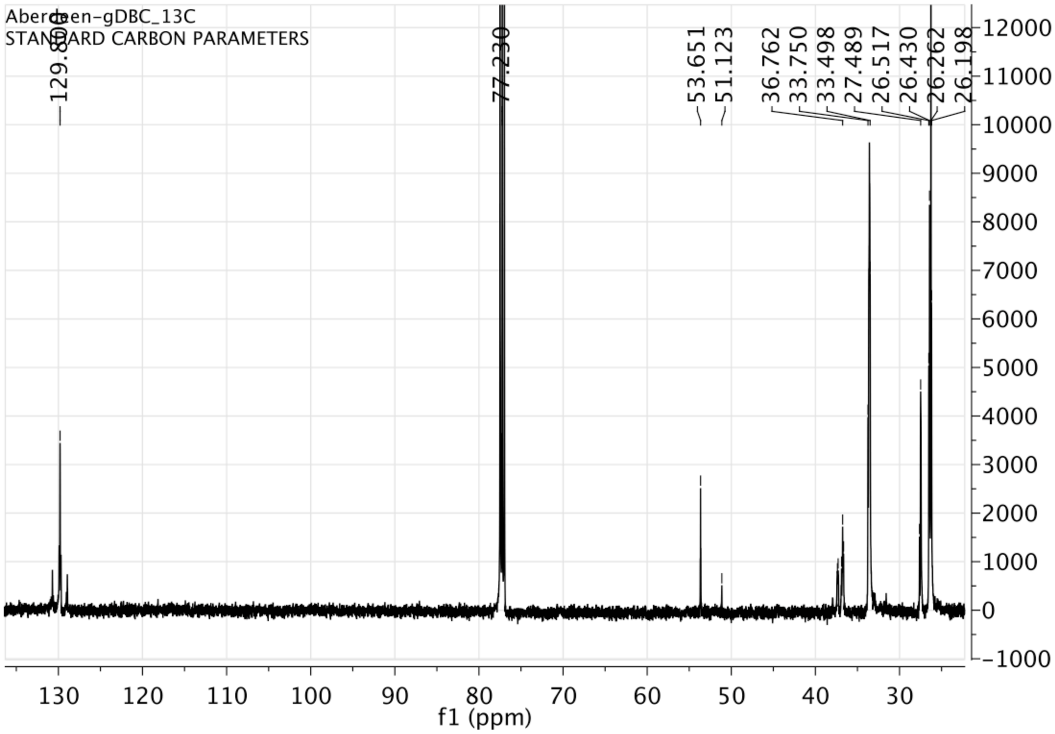


Figure S4. ^{13}C-NMR of 8.6x10^5 Da, 79 % *g*DBC-PB.

3.4×10^5 Da 76 % *gem*-dichlorocyclopropanated polybutadiene (*g*DCC-PB)

9.72 g (0.180 moles) *cis*-PB and 3.28 g (9.0 mmoles) CTAB were dissolved in 250 mL $CHCl_3$ and deoxygenated with bubbling N_2 for 30 minutes. To a separate round-bottomed flask was dissolved 50 g (.90 moles) KOH in 50 mL DI-H_2O and the solution was deoxygenated with bubbling N_2 for 30 minutes. After 30 minutes, the KOH solution as added dropwise to the PB solution and the reaction was allowed to proceed for 18 hours under a headspace of N_2. After 18 hours the solution was washed 3X with DI-H_2O, rotovapped to minimal volume and the polymer was precipitated with methanol. The polymer was reprecipitated twice more from CH_2Cl_2 with methanol and dried overnight on high vacuum. ^1H NMR (400 MHz, $CDCl_3$) d 5.46 (b, 2.00H), 5.05 (b, 0.16H), 2.18 (m, 4.0H), 1.62 (b, 20.1H) Traces of CH_3OH at 3.47 ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.63, 129.84, 129.74, 129.65, 128.93, 77.48, 77.23, 76.98, 65.55, 65.23, 32.84, 32.73, 32.66, 32.63, 27.55, 26.49, 25.25, 24.51, 24.49, 24.35, 24.30.

Copolymer composition = 22 % 1,4-PB, 2 % 1,2-PB, 76 % *g*DBC. Theoretical molecular weight calculated as follows: 1.6×10^5 Da PB starting material contains 2884 monomer units. Upon functionalization, the per monomer contribution to the polymer molecular weight increases from 54.09 Da to 137.01 Da (*g*DCC). For a functionalization of 76 %, then the final molecular weight is:

Molecular Weight = (0.76 * 2884 * 137.01) + (0.24 * 2884 * 54.09) = 3.4×10^5 Da

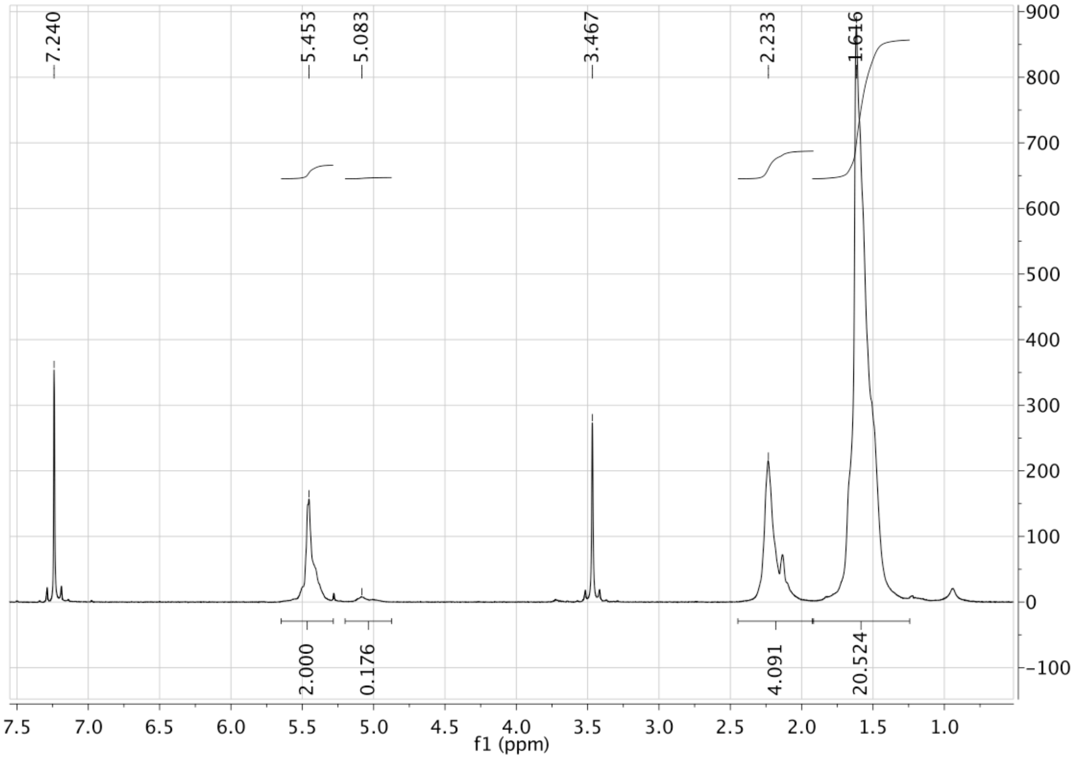


Figure S5. ^1H-NMR of 3.4×10^5 Da, 76 % *g*DCC-PB.

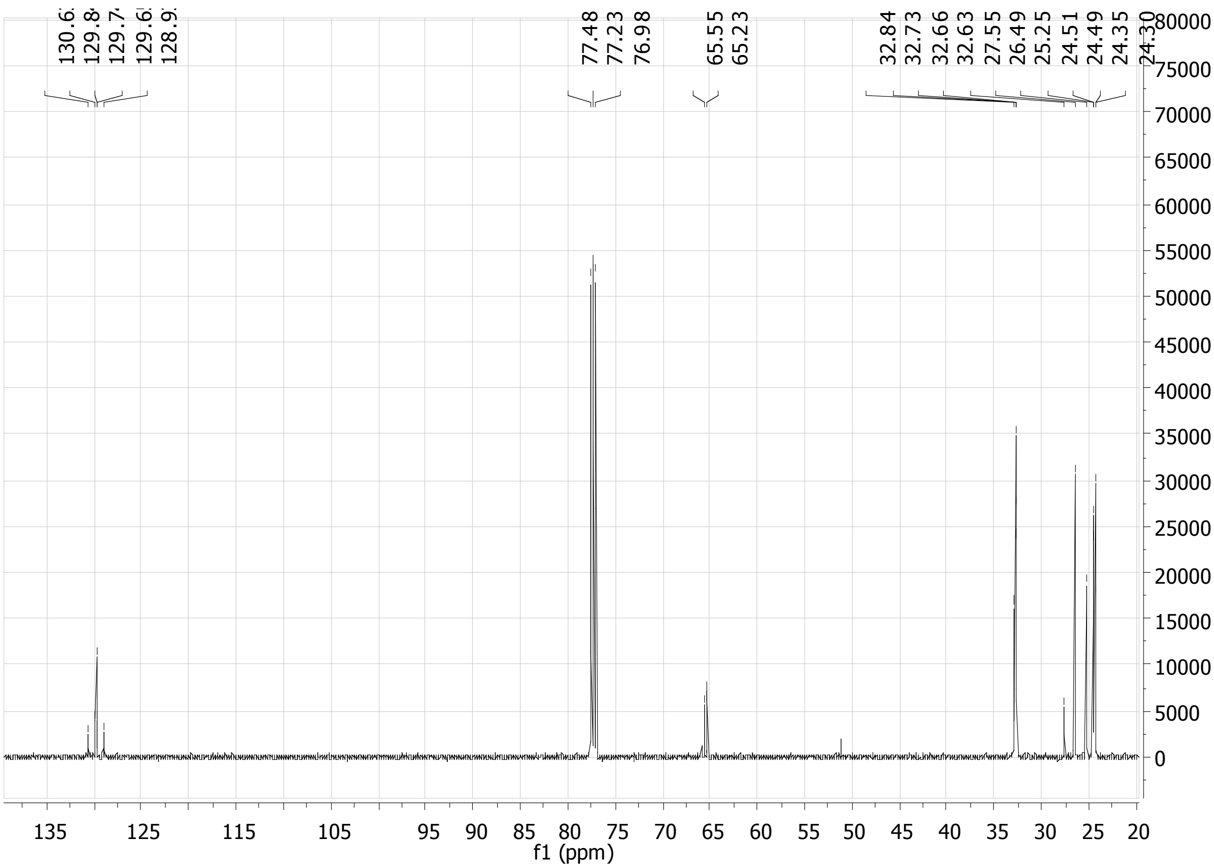


Figure S6. ^{13}C-NMR of 3.4x10^5 Da, 76 % *g*DCC-PB.

5.6x10^5 Da 80 % *gem*-bromochlorocyclopropanated polybutadiene (*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. ^{1}H NMR (400 MHz, $CDCl_3$) 5.47 (b, 2.00H); 5.06 (b, 0.20H); 2.26 (b, 4.5H); 1.62 (b, 29.6H). ^{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 = 5.6x10^5 Da, M_W = 1.0x10^6 Da, PDI = 1.79.

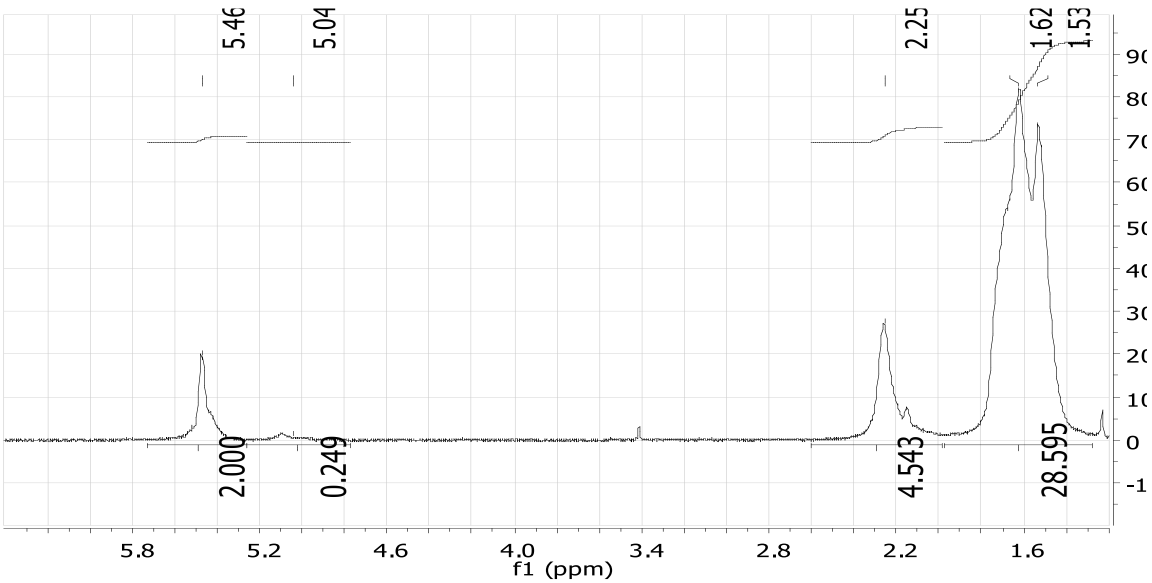


Figure S7. ^{1}H NMR of 5.6x10^{5} Da, 80 % *g*BCC-PB.

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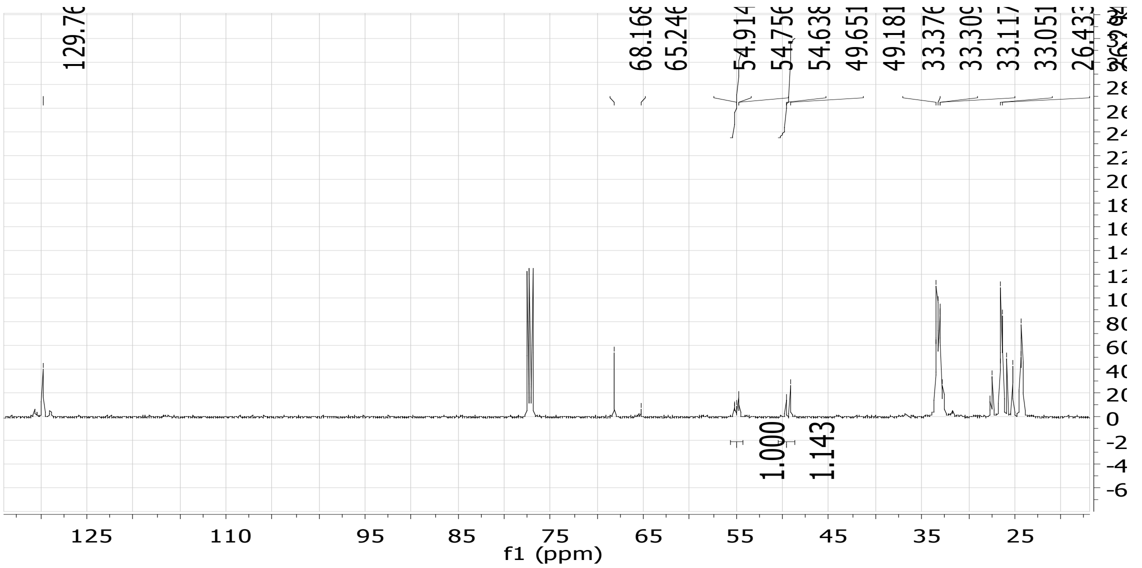

Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) of 80 % *cis*-*g*BCC-PB. *cis*-*syn*-Br isomer = 54.8 ppm; *cis*-*syn*-Cl isomer = 49.5 ppm. Residual THF observed at 68.2 ppm.

Extrusion Downward Force Profiles

The plots displayed in this section represent the downforce exerted by the melt over time and is used to compare relative melt viscosity between samples. This value is measured by an axial force transducer that is coupled with the extruder. The sharp reductions in force represent a time when the screws were stopped and a piece of polymer was removed for analysis. The polymer was then re-fed into the extruder as discussed in the experimental section of the paper.

$4.9\text{x}10^5$ Da 67 % *g*DBC-PB 60 °C and 100 rpm extrusion force profile

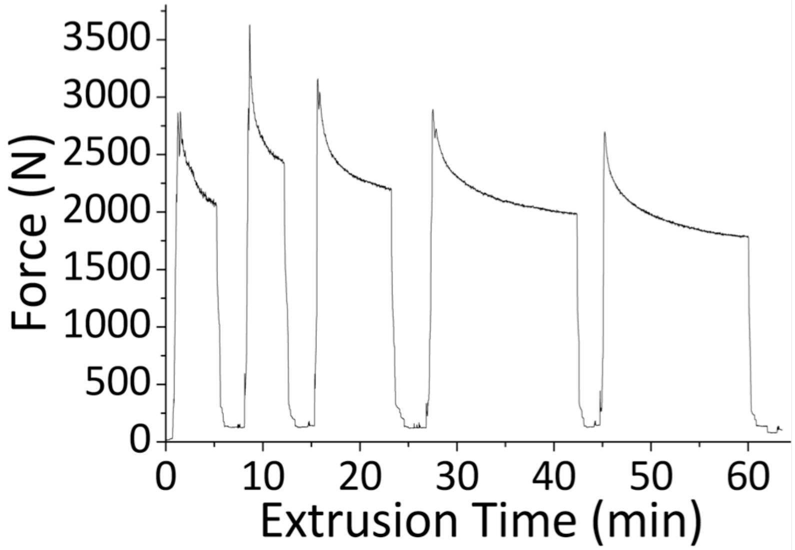

Figure S9. Force profile for extrusion of $4.9\text{x}10^5$ Da 67 % *g*DBC-PB at 60 °C and 100 rpm.

4.9×10^5 Da 67 % *g*DBC-PB 40 °C and 50 rpm extrusion force profile

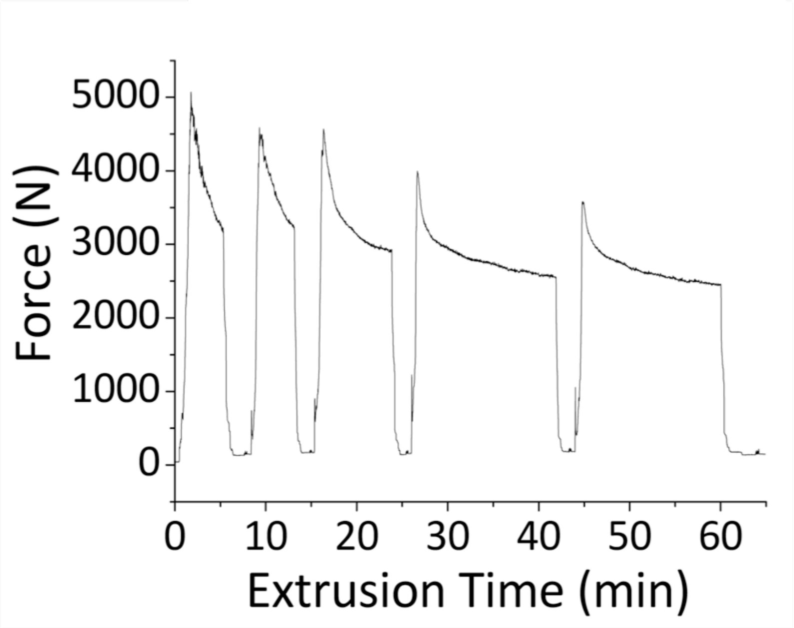

Figure S10. Force profile for extrusion of 4.9×10^5 Da 67 % *g*DBC-PB at 40 °C and 50 rpm.

8.6×10^5 Da 79 % *g*DBC-PB 60 °C and 50 rpm extrusion force profile

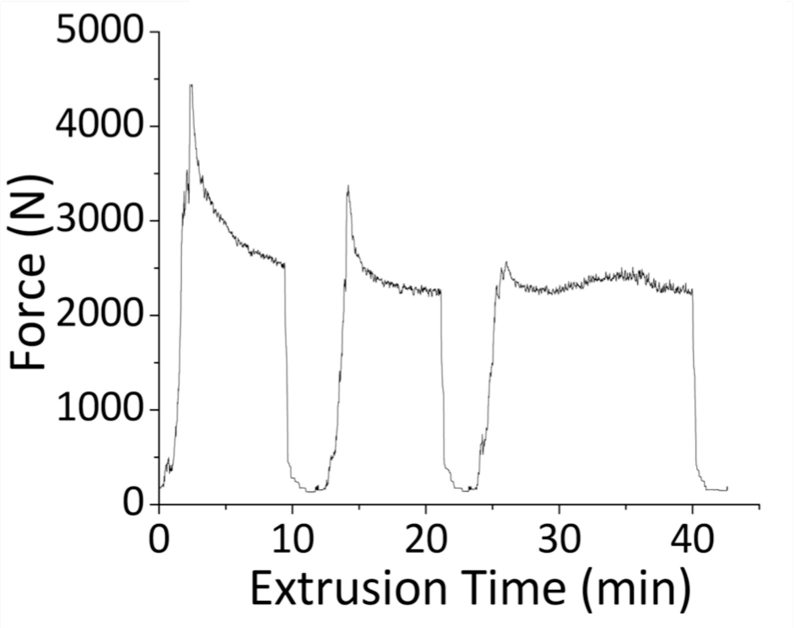

Figure S11. Force profile for extrusion of 8.6×10^5 Da 79 % *g*DBC-PB at 60 °C and 50 rpm.

3.4x10^5 Da 76 % *g*DCC-PB 60 °C and 100 rpm extrusion force profile

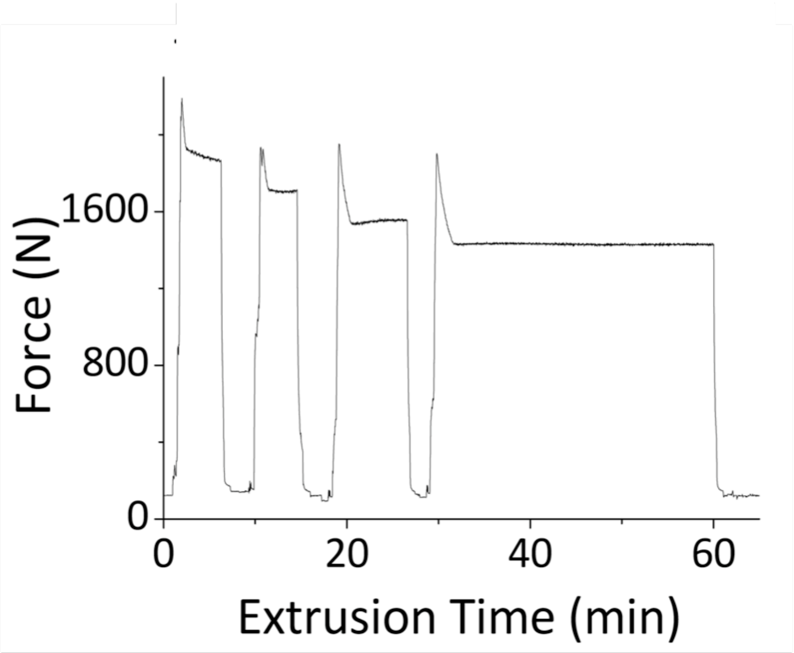

Figure S12. Force profile for extrusion of 3.4x10^5 Da 76 % *g*DCC-PB at 60 °C and 100 rpm.

5.6x10^5 Da 80 % *g*BCC-PB 40 °C and 50 rpm extrusion force profile

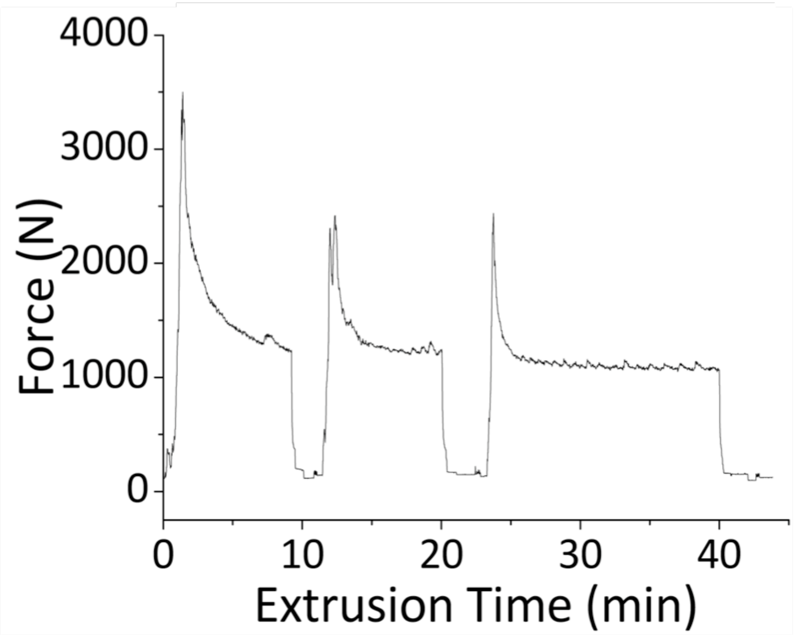

Figure S13. Force profile for extrusion of 5.6x10^5 Da 80 % *g*BCC-PB at 40 °C and 50 rpm.

$4.9x10^5$ Da 67 % *g*DBC-PB 60 °C and 100 rpm with nucleophile extrusion force profile

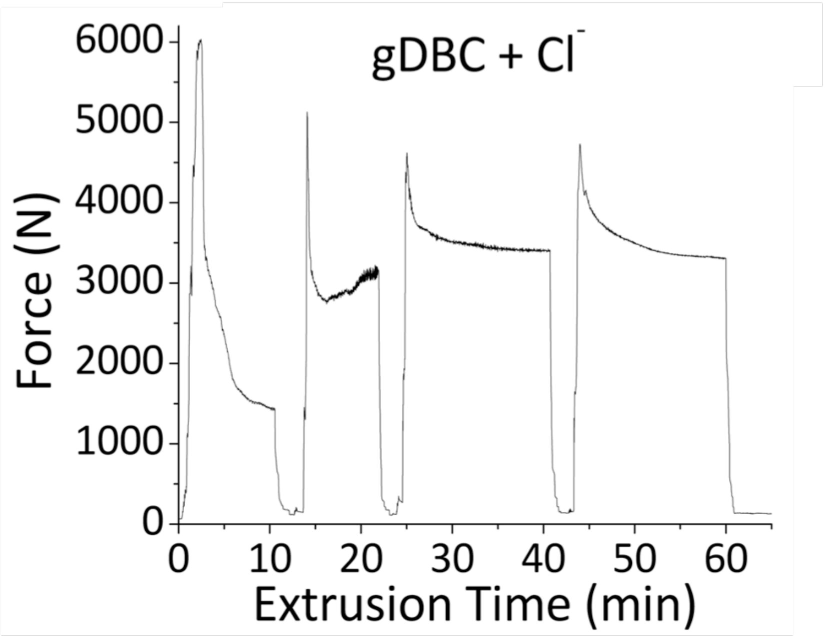

Figure S14. Force profile for extrusion of $4.9x10^5$ Da 67 % *g*DBC-PB at 60 °C and 100 rpm in the presence of benzyltriethylammonium chloride.

Extruded Polymer Characterization

4.9x10^5 Da 67 % *g*DBC-PB 60 °C and 100 rpm extrusion ring-opening

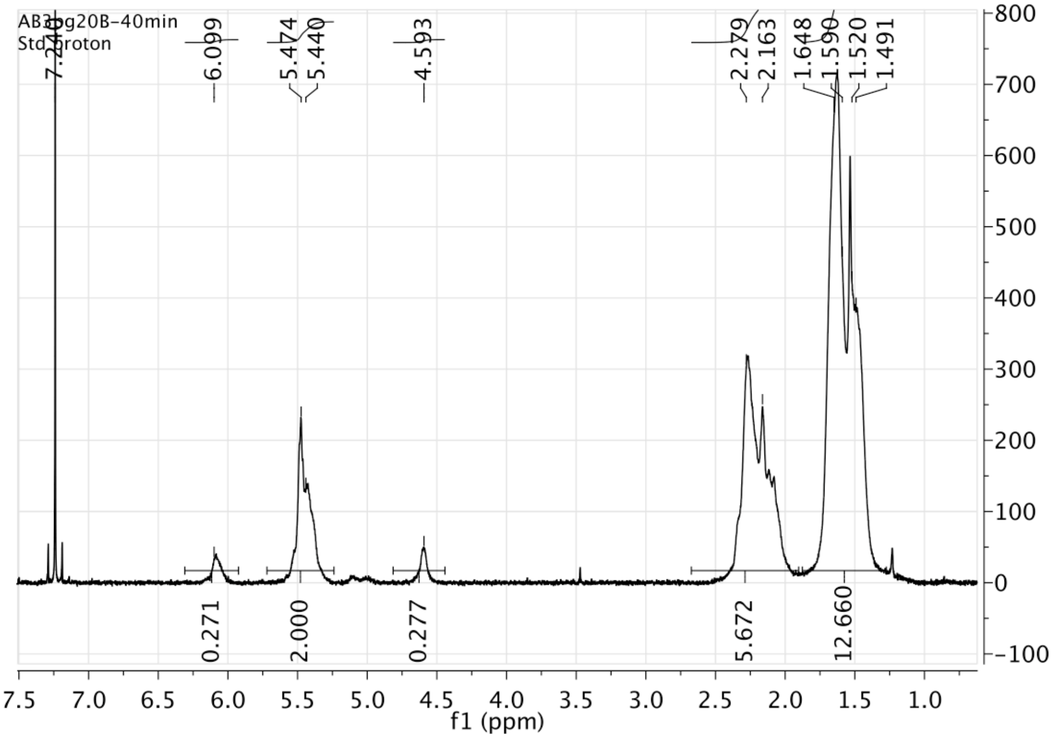

Figure S15. ^{1}H NMR of extruded 4.9x10^5 Da 67 % *g*DBC-PB at 60 °C and 100 rpm. Sample was extruded for 40 minutes. Resonances at 6.099 and 4.593 ppm correspond to the vinyl and allylic protons H_A and H_B, respectively, of the product dihaloalkene, as indicated in the main text.

4.9x10^5 Da 67 % *g*DBC-PB 40 °C and 50 rpm extrusion ring-opening

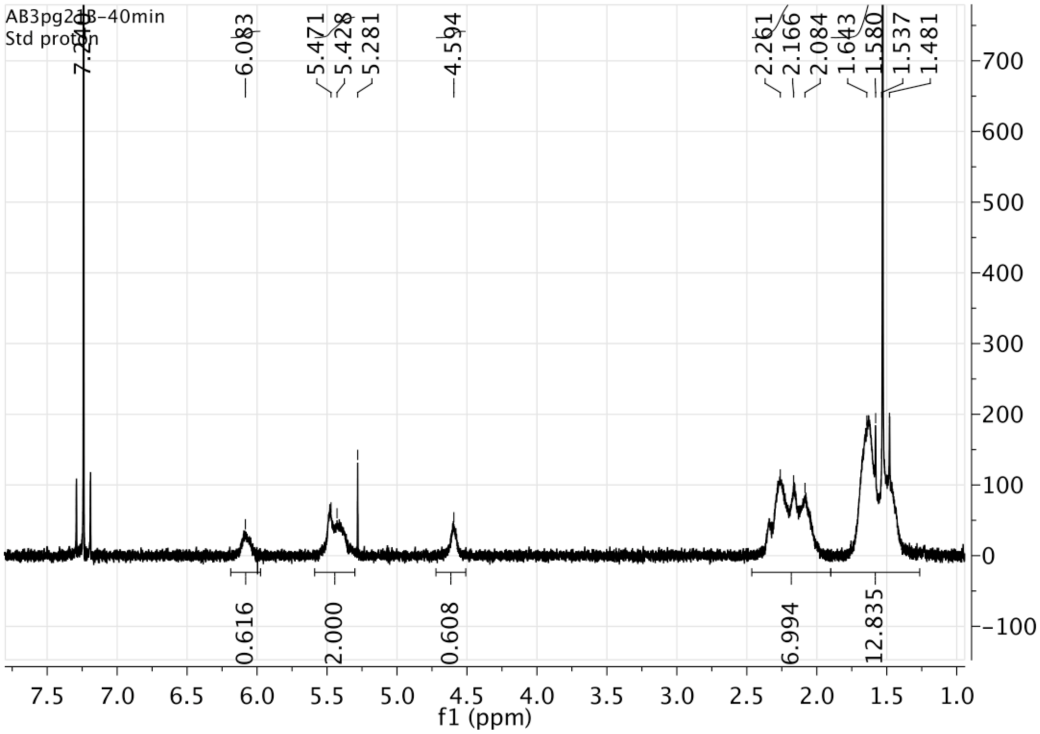

Figure S16. ^{1}H NMR of extruded 4.9x10^5 Da 67 % *g*DBC-PB at 40 °C and 50 rpm. Sample was extruded for 40 minutes. Resonances at 6.083 and 4.594 ppm correspond to the vinyl and allylic protons H_A and H_B, respectively, of the product dihaloalkene, as indicated in the main text. Trace CH_2Cl_2 present at 5.281 ppm.

8.6x10^5 Da 79 % *g*DBC-PB 60 °C and 50 rpm extrusion ring-opening

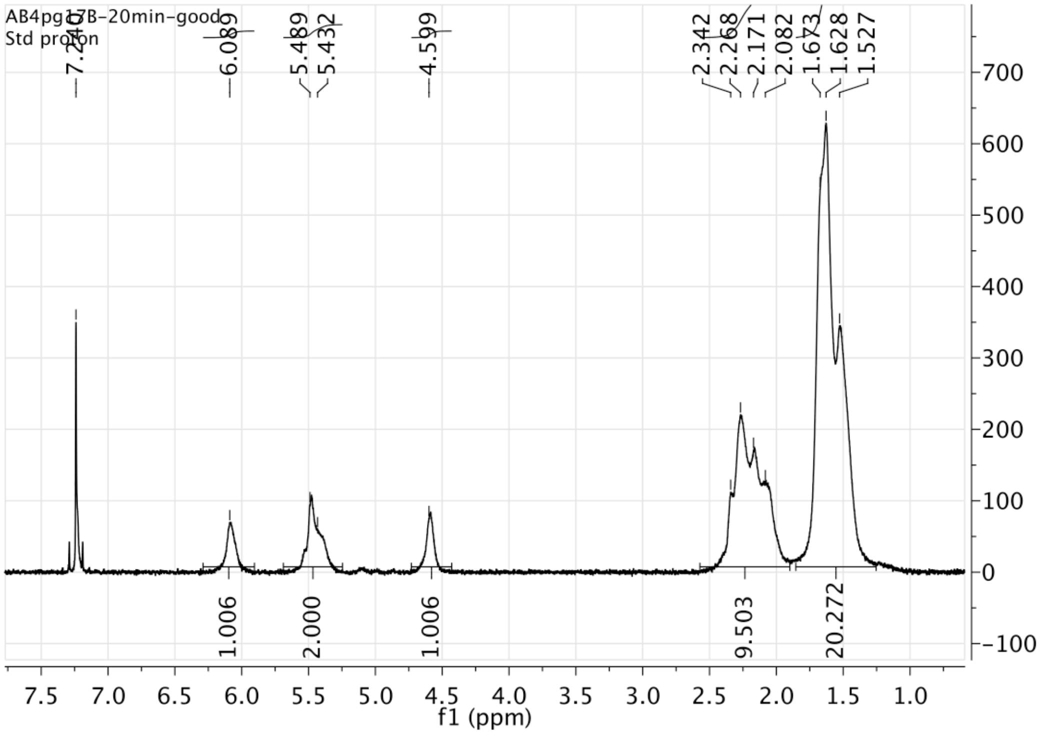

Figure S17. ^{1}H NMR of extruded 8.6x10^5 Da 79 % *g*DBC-PB at 60 °C and 50 rpm. Sample was extruded for 20 minutes. Resonances at 6.089 and 4.599 ppm correspond to the vinyl and allylic protons H_A and H_B, respectively, of the product dihaloalkene, as indicated in the main text.

$3.4\text{x}10^5$ Da 76 % *g*DCC-PB 60 °C and 100 rpm extrusion ring-opening

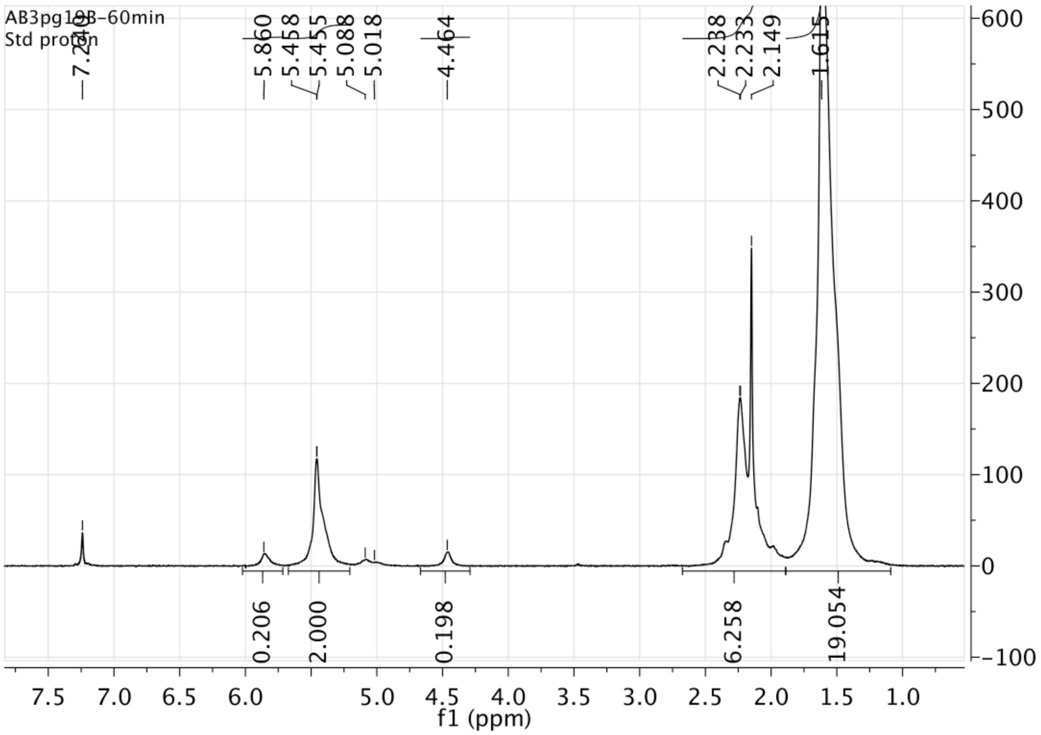

Figure S18. ^{1}H NMR of extruded $3.4\text{x}10^5$ Da 76 % *g*DCC-PB at 60 °C and 100 rpm. Sample was extruded for 60 minutes. Resonances at 5.860 and 4.464 ppm correspond to the vinyl and allylic protons H_A and H_B, respectively, of the product dihaloalkene, as indicated in the main text.

$5.6\text{x}10^5$ Da 80 % *g*BCC-PB 40 °C and 50 rpm extrusion force profile

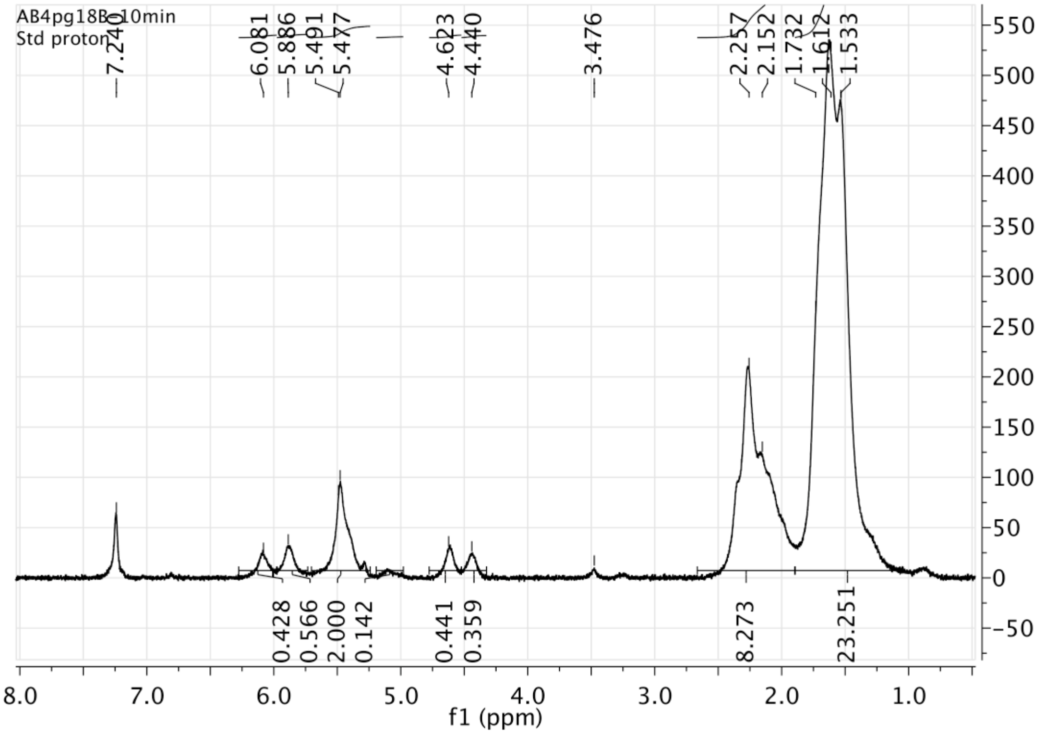

Figure S19. ^{1}H NMR of extruded $5.6\text{x}10^5$ Da 80 % *g*BCC-PB at 40 °C and 50 rpm. Sample was extruded for 10 minutes. Resonances at 6.081, 5.886, 4.623 and 4.440 ppm correspond to the vinyl and allylic protons, respectively, of the product dihaloalkene, as indicated in the main text.

6.081 ppm represents H_C in Figure 3, 5.886 ppm represents H_A, 4.623 ppm represents H_B and 4.440 ppm represents H_D. Trace CH_3OH present at 3.476 ppm.

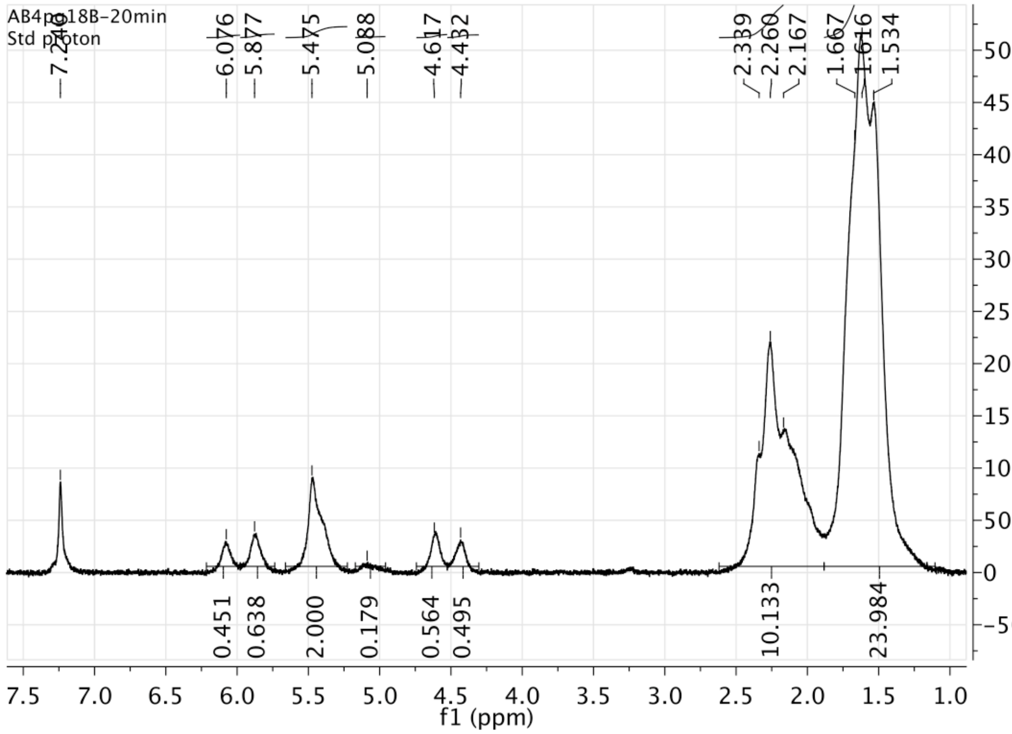

Figure S20. ^{1}H NMR of extruded 5.6x10^5 Da 80 % *g*BCC-PB at 40 °C and 50 rpm. Sample was extruded for 20 minutes. Resonances at 6.076, 5.877, 4.617 and 4.432 ppm correspond to the vinyl and allylic protons, respectively, of the product dihaloalkene, as indicated in the main text.

6.076 ppm represents H_C in Figure 3, 5.877 ppm represents H_A, 4.617 ppm represents H_B and 4.432 ppm represents H_D.

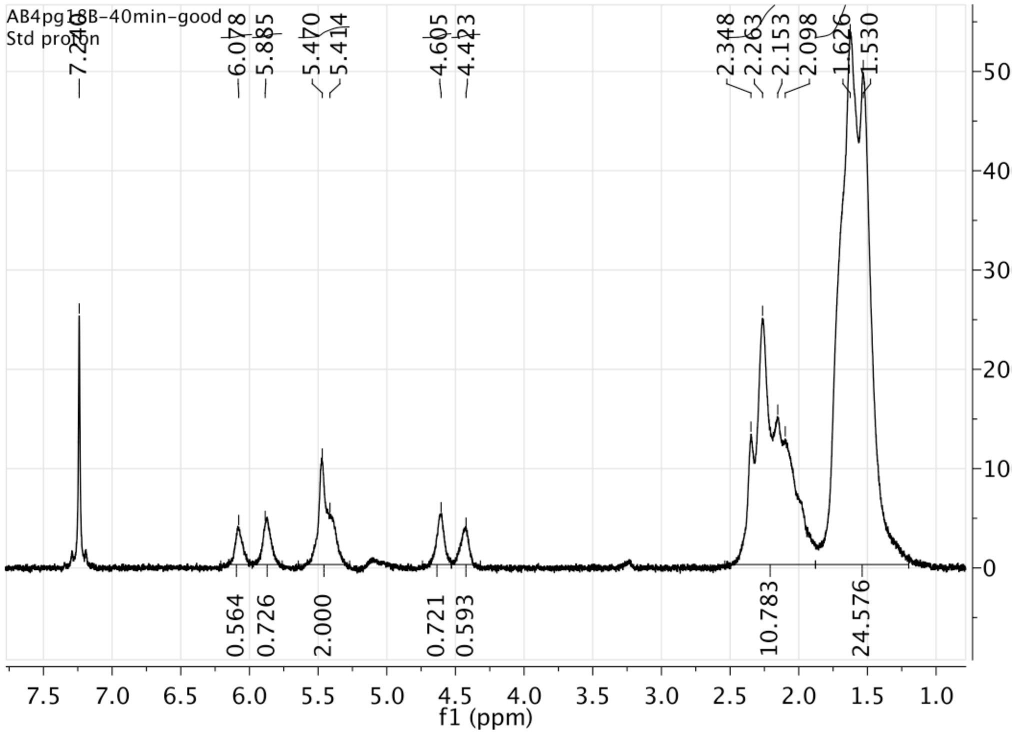

Figure S21. ^{1}H NMR of extruded 5.6x10^5 Da 80 % *g*BCC-PB at 40 °C and 50 rpm. Sample was extruded for 40 minutes. Resonances at 6.078, 5.885, 4.605 and 4.423 ppm correspond to the vinyl and allylic protons, respectively, of the product dihaloalkene, as indicated in the main text.

6.078 ppm represents H_C in Figure 3, 5.885 ppm represents H_A, 4.605 ppm represents H_B and 4.423 ppm represents H_D.

4.9x10^5 Da 67 % *g*DBC-PB 60 °C and 100 rpm with nucleophile extrusion ring-opening

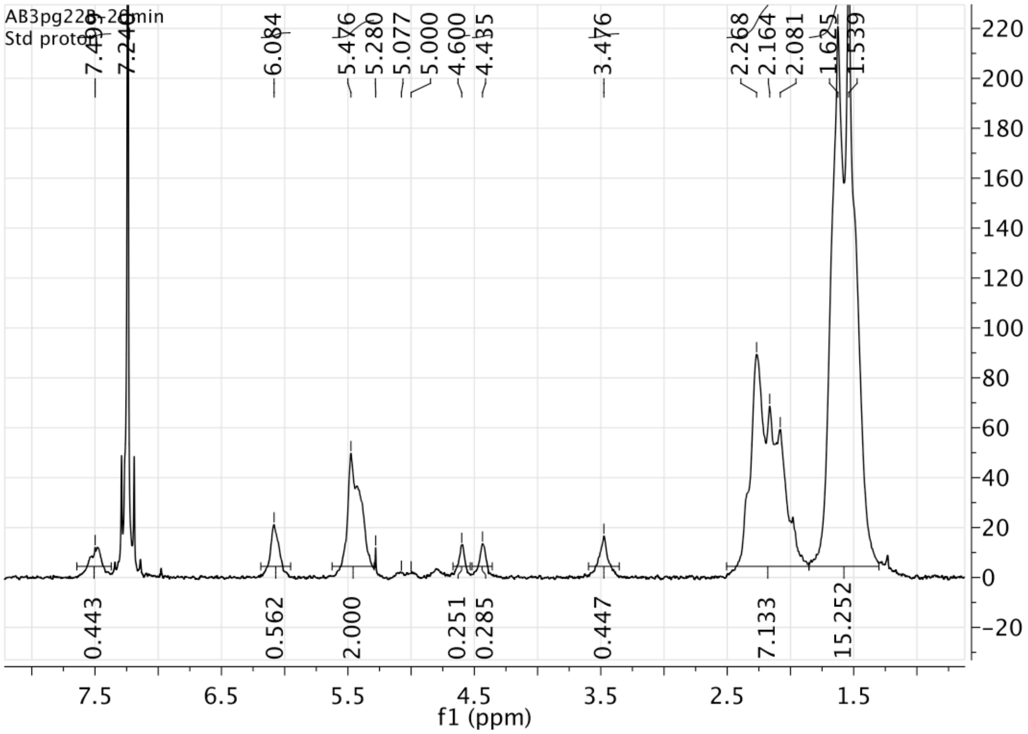

Figure S22. ^{1}H NMR of extruded 4.9x10^5 Da 67 % *g*DBC-PB at 60 °C and 100 rpm in the presence of 1.2 equivalents (to ring opened monomer) of benzyltriethylammonium chloride. Sample was extruded for 20 minutes. Resonances at 6.084 and 4.600 ppm correspond to the vinyl and allylic protons, H_A and H_B, respectively, of the product dihaloalkene, as indicated in the main text.
Resonance at 4.435 ppm represents nucleophilic displacement of allylic bromide with chloride ion. The percent displacement is calculated based upon the comparison of 4.600 and 4.435 ppm peak. Trace CH_3OH at 3.476 ppm as well as unreacted benzyltriethylammonium ion at 7.499 ppm and 3.476 ppm.

Nucleophile Incorporation Control Experiment

To achieve ring-opening, a 9.35 mg/mL solution of 88 % *g*DBC-PB polymer in BHT-free THF was sonicated on a Vibracell Model VCX500 sonicator operating at 20 kHz for 30 min. The solution remained in an ice water bath and under N_2 during a pulsed (1 second on/ 1 second off) ultrasonication sequence. 108.2 mg of the 50 % ring-opened polymer was dissolved in 10 mL of CH_2Cl_2 along with 1.2 eq (based on moles of opened *g*DBC monomer) of benzyltriethylammonium chloride. This was let stir vigorously at room temperature for 4 hours. This exactly mimics the times and concentrations present during work-up of the extruded material. The work-up consisted of rotovapping to minimal volume, precipitating from CH_3OH and drying. The percent displacement from this reaction is 13.2% which is 75 % of the 53.5 % displacement observed in the extrusion experiment.
For more details on sonication experiments please see reference 7.

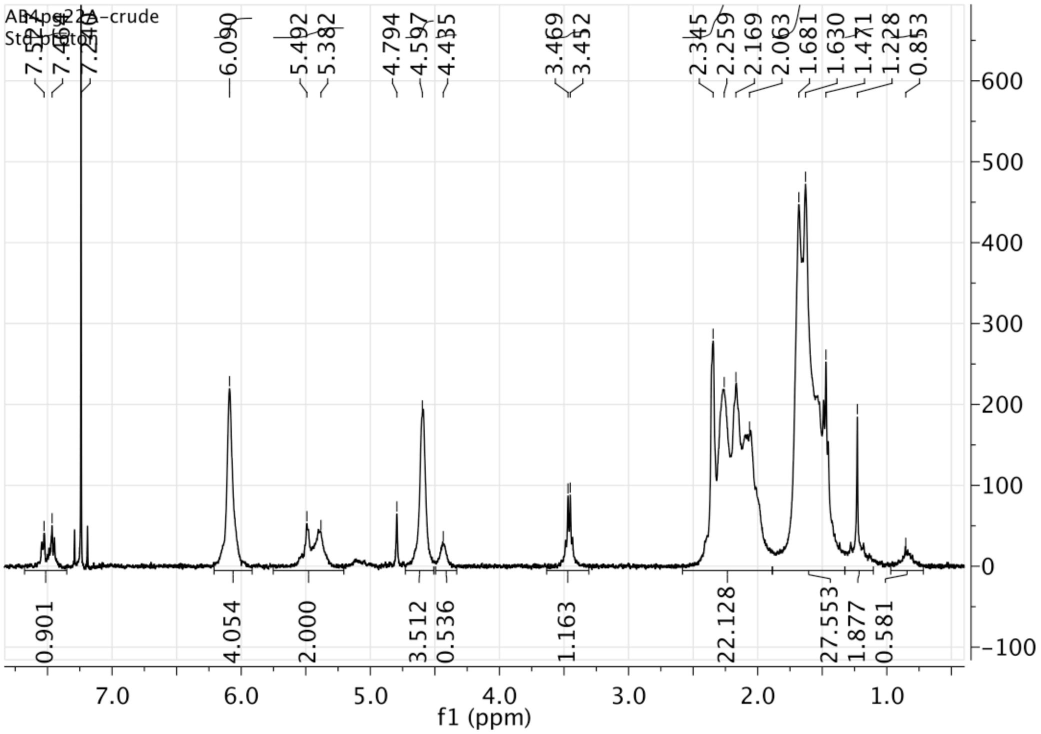

Figure S23. ^{1}H NMR of sonicated 88 % *g*DBC-PB then stirred in the presence of 1.2 equivalents (to ring opened monomer) of benzyltriethylammonium chloride. Sample let stir for 4 hours in CH_2Cl_2 to mimic workup conditions of extruded polymers. Resonances at 6.084 and 4.600 correspond to the vinyl and allylic protons H_A and H_B, respectively, of the product dihaloalkene, as indicated in the main text.
Resonance at 4.435 ppm represents nucleophilic displacement of allylic bromide with chloride ion. The percent displacement is calculated based upon the comparison of 4.600 and 4.435 ppm peak. Trace CH_3OH at 3.476 ppm as well as unreacted benzyltriethylammonium ion at 7.499 ppm and 3.476 ppm. Trace impurity at 4.794 ppm.

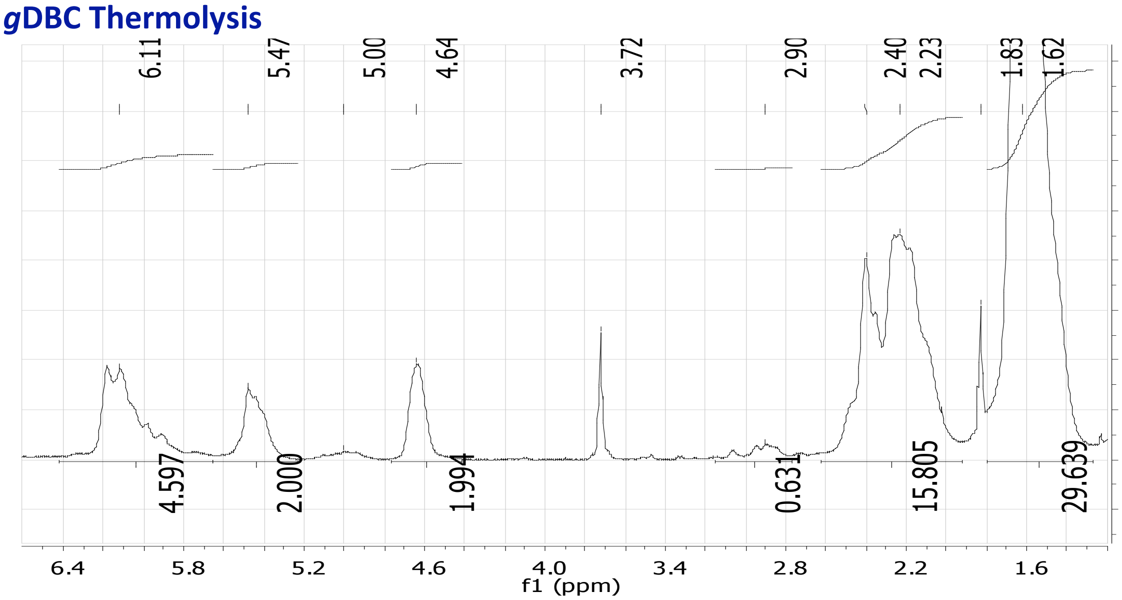

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) after thermolysis of *g*DBC polymer (165 ºC, 17 hours methyl benzoate, N_2) indicates formation of both 2,3-dibromoalkene products (6 ppm, 4.64 ppm) in addition to elimination side reactions as a result of thermal activation (6.4 – 5.6 ppm).