

# Supporting Online Material for

## Reactive Cross-talk Between Adjacent Tension-Trapped Transition States

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### Table of Contents

Experimental .....	3
Polymer Scission Cycle .....	4
Synthesis .....	5
Trimethylsilyl fluorosulfonyldifluoroacetate (TFDA).....	5
192 kDa 8.0 % <i>c/t</i> -gDFC-PB [TFDA] .....	6
96.8 kDa 3.8 % <i>c/t</i> -gDFC-PB .....	8
179 kDa 9.1 % <i>c/t</i> -gDFC-PB .....	10
154 kDa 10.9 % <i>c/t</i> -gDFC-PB .....	11
190 kDa 22.0 % <i>c/t</i> -gDFC-PB .....	13
319 kDa 32.4 % <i>c/t</i> -gDFC-PB .....	14
275 kDa 36.1 % <i>c/t</i> -gDFC-PB .....	16
173 kDa 47.4 % <i>c/t</i> -gDFC-PB .....	18
290 kDa 51.7 % <i>c/t</i> -gDFC-PB .....	19
88.4 kDa 58.7 % <i>c/t</i> -gDFC-PB .....	21
177 kDa 95.1 % <i>c/t</i> -gDFC-PB .....	23
(4Z,8Z)-13,13-Difluoro-bicyclo[10.1.0]trideca-4,8-diene     and     (9E)-5,5,14,14-tetrafluoro- tricyclo[11.1.0.0 <sup>4,6</sup> ]tetradec-9-ene .....	24
65.5 kDa 33.3 % <i>trans</i> -gDFC-PB [ROMP] .....	25
66.2 kDa 66.7 % <i>trans</i> -bis-gDFC-PB [ROMP] .....	28
261 kDa <i>c/t</i> -[36.1 % gDFC / 26.2 % gDCC]-PB .....	30
Ultrasound Experiments.....	32
96.8 kDa 3.8 % <i>c/t</i> -gDFC-PB .....	32

192 kDa 8.0 % <i>c/t</i> -gDFC-PB .....	33
179 kDa 9.1 % <i>c/t</i> -gDFC-PB .....	34
154 kDa 10.9 % <i>c/t</i> -gDFC-PB .....	35
190 kDa 22.0 % <i>c/t</i> -gDFC-PB .....	36
319 kDa 32.4 % <i>c/t</i> -gDFC-PB .....	37
275 kDa 36.1 % <i>c/t</i> -gDFC-PB .....	38
173 kDa 47.4 % <i>c/t</i> -gDFC-PB .....	39
290 kDa 51.7 % <i>c/t</i> -gDFC-PB .....	40
88.4 kDa 58.7 % <i>c/t</i> -gDFC-PB .....	41
177 kDa 95.1 % <i>c/t</i> -gDFC-PB .....	42
65.5 kDa 33.3 % <i>trans</i> -gDFC-PB [ROMP] .....	43
66.2 kDa 66.7 % <i>trans</i> -gDFC-PB [ROMP] .....	44
261 kDa <i>c/t</i> -[36.1 % gDFC / 26.2 % gDCC]-PB .....	45
Product Analysis: Coupled Diradical Disproportionation .....	46
<i>cis/trans</i> -PB .....	46
275 kDa 36 % <i>c/t</i> -gDFC-PB ))) , 3 hours .....	47
<sup>19</sup> F-NMR .....	49
Reference Compounds .....	49
177 kDa 95 % <i>c/t</i> -gDFC-PB .....	52
36 % ))) vs. 95 % ))) .....	56
<sup>1</sup> H NMR .....	56
<sup>19</sup> F NMR .....	57
Table of gDFC Activation .....	58
Computational Work .....	59
Theory .....	59
Simulation Details .....	59
Supplementary AI-SMD Results .....	60
References .....	61

## Experimental

Unless otherwise stated, all starting materials and reagents were obtained from commercial suppliers and used without further purification. Polybutadiene (*cis* and *trans*; 36 % *cis*, 55 % *trans*, 9 % 1,2 addition, referred to herein as *c/t*-PB), sodium chlorodifluoroacetate, methyl benzoate, 1.0 M hydrochloric acid in diethyl ether and 4 Å molecular sieves (beads, 4-8 mesh) were purchased from Sigma-Aldrich. CDCl<sub>3</sub> was obtained from Cambridge Isotope Laboratories (D, 99.8%), CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> from BDH. *Trans,trans,trans*-1,5,9-cyclododecatriene (90% with 10% phenol stabilizer, Alfa Aesar) was dissolved in diethyl ether, washed with saturated aqueous sodium bicarbonate solution, separated, concentrated under reduced pressure, and stored as a stock solution in toluene or methyl benzoate over 4 Å molecular sieves (beads, 4-8 mesh) for 12 hours prior to ROMP or difluorocyclopropanation reactions, respectively. [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-[2-[[4-methylphenyl]imino]methyl]-4-nitrophenolyl]-[3-phenyl-1H-inden-1-ylidene]ruthenium(II) chloride (Ru\* below) was ordered from Strem and diluted with toluene and used as a stock solution. Elemental analysis of the ROMP monomers was performed by Complete Analysis Laboratories.

Gel permeation chromatography (GPC) was performed on a single column (Agilent Technology PL gel, #179911GP-504, 10<sup>4</sup> Å) using inhibitor-free tetrahydrofuran (THF) as mobile phase at 1 mL min<sup>-1</sup> at room temperature. The flow rate was set using a Varian Prostar Model 210 pump, and molecular weights were calculated using an inline Wyatt Dawn EOS multi-angle light scattering (MALS) detector, Wyatt quasi-electric light scattering (QELS) and Wyatt Optilab DSP Interferometric Refractometer (RI). The dn/dc values for each polymer were determined by injecting a known amount of polymer and back-calculating the appropriate value.

Ultrasound experiments were performed in inhibitor-free THF on a Vibracell Model VCX500 operating at 20 kHz with a 13.1 mm replaceable titanium tip probe from Sonics and Materials (<http://www.sonics.biz/>). Each sonication was performed on 1.5 mg mL<sup>-1</sup> polymer solutions in ~15 mL of THF deoxygenated with bubbling N<sub>2</sub> for 30 minutes prior to sonication at 6-9 °C in an ice-water bath at 30% amplitude (11.9 W cm<sup>-2</sup>) and the sonication pulse was set to 1 s on / 1 s off. <sup>1</sup>H-, <sup>19</sup>F- and <sup>13</sup>C-analyses were conducted on either a 400 MHz or 500 MHz Varian spectrophotometer and the residual solvent peak (7.240 ppm [<sup>1</sup>H], 77.23 ppm [<sup>13</sup>C]) was used as the chemical shift reference.

## Polymer Scission Cycle

All data obtained in the mechanical isomerization of *cis*- to *trans*-gDFCs is treated by obtaining the % isomerization versus the polymer scission cycle. Molecular weights are taken from GPC-MALS data.

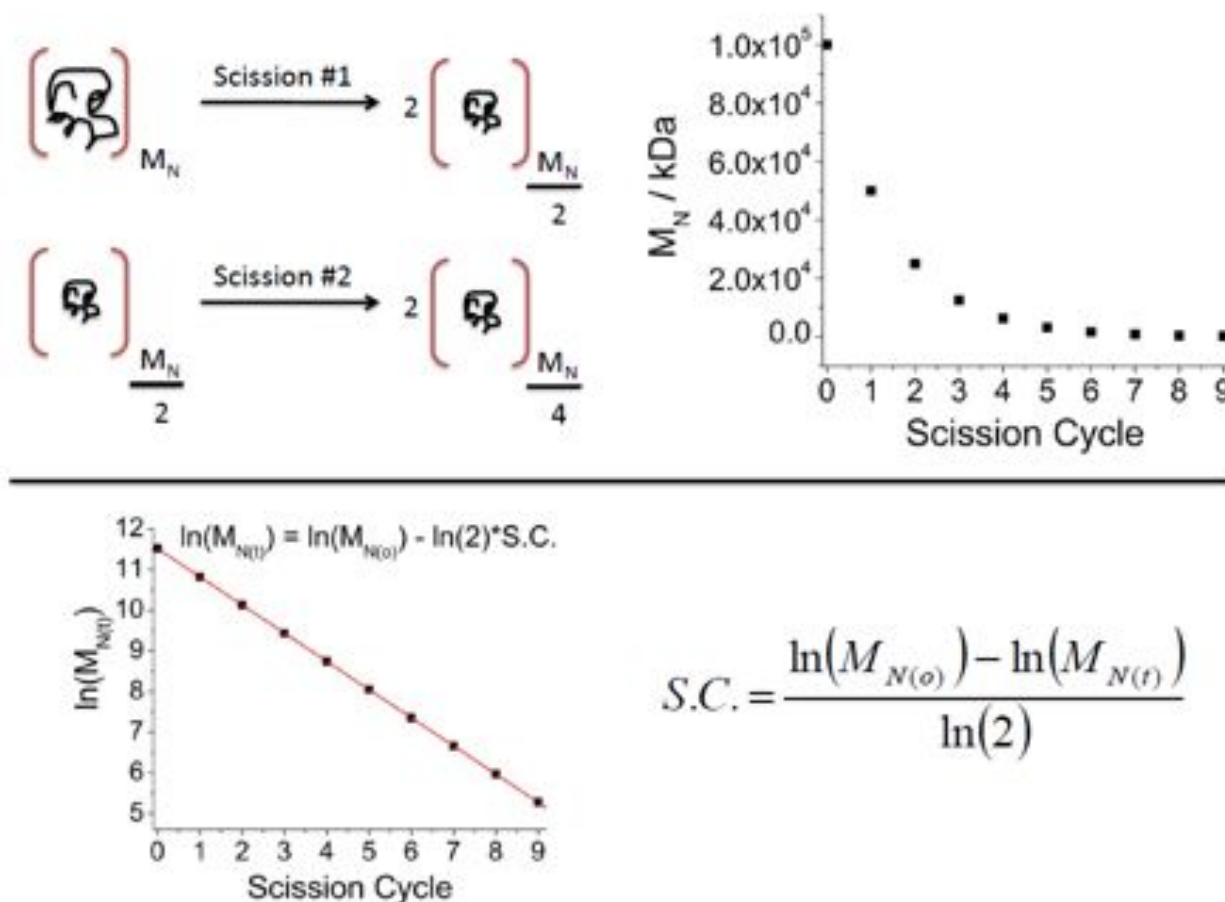


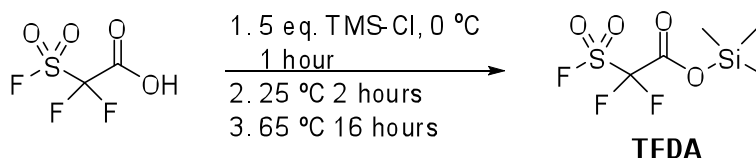
Figure S1: Sonochemically, polymer chains are selectively cleaved near the polymer midpoint. Schematically this is shown in the top left. The resulting molecular weight profile after a given ‘scission cycle’ (S.C.) is shown in the plot at the top right using an initially 100 kDa polymer assuming direct halving. Taking the natural log of the molecular weight at intervals of the scission is thus linear with the equation noted in the bottom left. Solving for the scission cycle is therefore completed by using the rearranged equation in the bottom right of the scheme.

Here  $M_{N(0)}$  denotes the initial number-averaged molecular weight and  $M_{N(t)}$  is the molecular weight after a given time (t) of sonication.

## Synthesis

Syntheses of *gem*-difluorocyclopropanated polybutadiene copolymers (gDFC-PBs) of 3.8 %-, 10.9 %-, 32.4 %-, 36.1 %-, 51.7 %- and 58.7 %-gDFC were prepared by the pyrolysis of sodium chlorodifluoroacetate in dry methyl benzoate at 190 °C. An initial attempt at synthesizing a gDFC-PB copolymer with trimethylsilyl fluorosulfonyldifluoroacetate (TFDA)<sup>1</sup> was attempted and resulted in the 8.0 % *c/t*-gDFC-PB copolymer. Pyrolysis of sodium chlorodifluoroacetate in dry methyl benzoate proved to be a more facile route for polybutadiene functionalization. For small molecule ROMP monomers, TFDA served as the sole reagent for gDFC preparation.

### Trimethylsilyl fluorosulfonyldifluoroacetate (TFDA)



A 3-necked, oven-dried round-bottomed flask with magnetic stirrer, N<sub>2</sub> inlet, dropping funnel and water-cooled reflux condenser leading to an empty 500 mL backup trap containing CaCl<sub>2</sub> was prepared. The backup trap was connected as the N<sub>2</sub> outlet by tygon tubing to an inverted glass funnel that was positioned just above a beaker containing 60 g of NaHCO<sub>3</sub> in 200 mL of water. To the round-bottomed flask was added 5 mL (48.4 mmol) of 2,2-difluoro-2-(fluorosulfonyl)acetic acid and the flask was cooled to 0 °C with an ice/water bath. When the temperature equilibrated, 31 mL (244 mmol, 5 equivalents) chlorotrimethylsilane (TMS-Cl) was added to the dropping funnel. TMS-Cl was allowed to mix in the flask by slow addition over one hour at 0 °C then the ice/water bath was removed and the reaction was allowed to proceed for an additional two hours. After two hours, an oil bath was placed under the reaction and heated to 65 °C; the reaction was allowed to proceed at reflux overnight (~ 16 hours). After 16 hours the excess TMS-Cl was removed by distillation at 30 °C resulting in a colorless oil as the product (8.4 g, 69% yield). The product was checked by <sup>19</sup>F-NMR and matched the spectrum from the literature.<sup>1</sup> <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ 41.14 (t, 1F, *J* = 5.1 Hz), -103.2 (d, 2F, *J* = 5.1 Hz). Due to the instability of TFDA to hydrolysis, the reagent was used directly after preparation and without further characterization.

### 192 kDa 8.0 % *c/t*-gDFC-PB [TFDA]

0.5 g (9.24 mmol) *c/t*-PB was dissolved in 50 mL CHCl<sub>3</sub>, rotovapped to dryness and dried for 2 hours at 60 °C in a round-bottomed flask with magnetic stirrer. After drying, 0.032 g (0.76 mmol) NaF was quickly added to the flask, a water-cooled reflux condenser with N<sub>2</sub> inlet, then dry toluene:methyl benzoate (75 mL: 75 mL) and the *c/t*-PB was stirred until completely dissolved. After dissolved, the *c/t*-PB solution was heated to 120 °C with an oil bath under N<sub>2</sub> and 2.3 g (9.2 mmol) TFDA was added dropwise (by syringe pump) over 2 hours. After complete addition, toluene was removed by distillation, the polymer solution was washed 3X with DI-H<sub>2</sub>O and product was precipitated with methanol. The polymer was reprecipitated with methanol twice more from minimal CHCl<sub>3</sub> and dried overnight on high vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.40 (b, 2.00H), 4.94 (m, 0.24H), 2.05 (b, 4.17H), 1.7-1.0 (0.82H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -124.8 (d, 1F, *J* = 153 Hz), -139.2 (t, 2.18F, *J* = 45.0 Hz), -154.3 (dt, 0.88F, *J* = 45.0 Hz, 155 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 142.86, 131.47, 131.08, 130.46, 130.34, 130.22, 130.05, 129.83, 129.64, 129.52, 129.39, 128.94, 128.73, 128.56, 128.10, 114.55, 114.46, 77.48, 77.23, 76.98, 43.96, 43.85, 38.41, 34.49, 34.34, 34.18, 32.93, 32.90, 32.39, 32.13, 30.43, 30.36, 28.13, 27.75, 27.61, 27.54, 27.10, 26.92, 25.20, 25.10, 24.68, 24.60, 21.95. Copolymer composition = 82.0% 1,4-PB; 10.0 % 1,2-PB; 8.0% gDFC (3.7 % *cis*-gDFC, 4.3 % *trans*-gDFC). MALS-GPC (dn dc<sup>-1</sup> = 0.1170); M<sub>N</sub> = 192,000 g mol<sup>-1</sup>, M<sub>W</sub> = 298,000 g mol<sup>-1</sup>, PDI = 1.55.

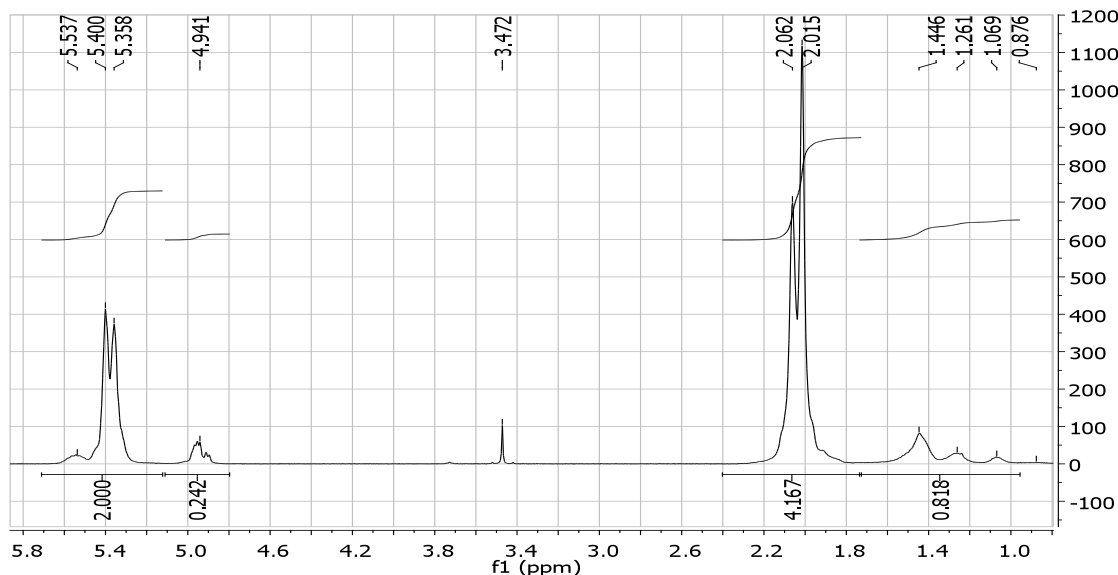


Figure S2: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 192 kDa 8.0% *c/t*-gDFC-PB.

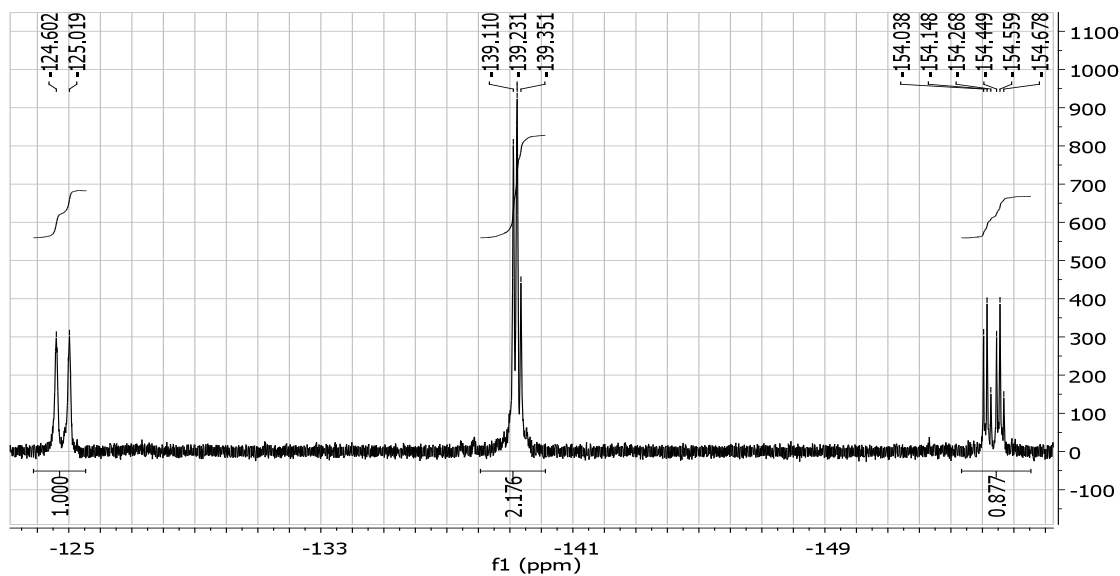


Figure S3:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 192 kDa 8.0 % *c/t*-gDFC-PB.

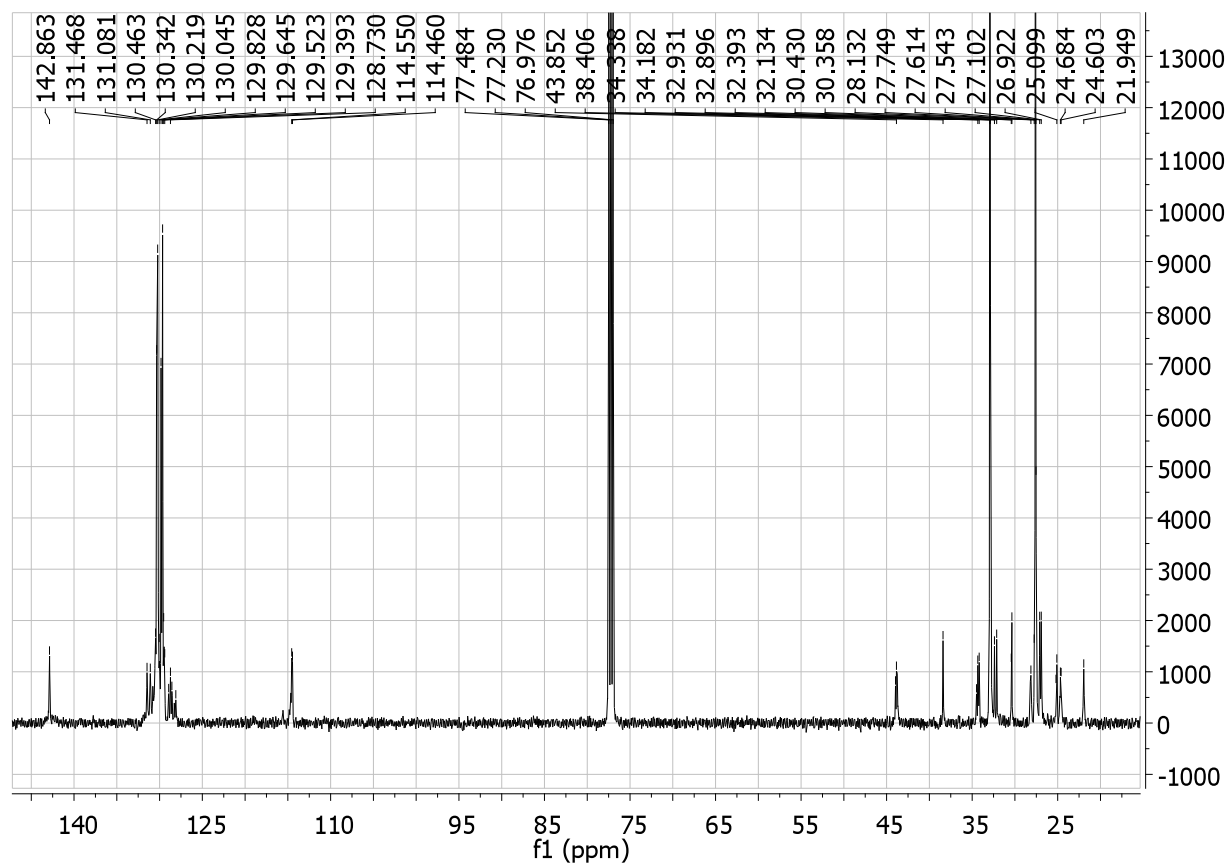


Figure S4:  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) of 192 kDa 8.0 % *c/t*-gDFC-PB.

### 96.8 kDa 3.8 % *c/t*-gDFC-PB

0.600 g (11.1 mmoles) of *c/t*-PB was dissolved in 100 mL methyl benzoate, 4 Å molecular sieves were added to the solution, and nitrogen was bubbled through the solution overnight. 0.17 g (1.12 mmoles) of sodium chlorodifluoroacetate was dissolved in 10 mL methyl benzoate, 4 Å molecular sieves were added to the solution, and nitrogen was bubbled through the solution overnight. After 16 hours of drying over molecular sieves, the PB solution was added by syringe to an oven dried round bottom flask under nitrogen and heated to 190 °C. Once the solution reached 190 °C, the sodium chlorodifluoroacetate solution was added dropwise over 1 hour by syringe pump. After complete addition, the reaction was allowed to proceed for an additional 15 minutes, was removed from the heat and allowed to cool. The reaction was washed 3 times with DI-water and the polymer was precipitated with methanol. The polymer was redissolved in dichloromethane, precipitated again with methanol, and allowed to dry on a high vac overnight.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.95 (b, 0.24H), 2.05 (b, 4.03H), 1.7-1.0 (m, 0.50H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.8 (d, 1F,  $J = 153$  Hz), -139.4 (t, 2.36F,  $J = 45.0$  Hz), -154.3 (dt, 0.97F,  $J = 45.0$  Hz, 155 Hz).  $^{13}\text{C}$  NMR (126 MHz,  $\text{cdcl}_3$ )  $\delta$  142.85, 131.46, 130.33, 130.21, 129.82, 129.63, 128.72, 128.55, 114.53, 77.48, 77.23, 76.98, 68.18, 43.83, 38.39, 34.33, 34.18, 32.92, 32.38, 30.42, 30.34, 27.74, 27.61, 27.10, 26.92, 25.83, 25.09, 24.68, 21.93. Copolymer composition = 85.7 % 1,4-PB; 10.5 % 1,2-PB; 3.8% gDFC (1.7 % *cis*-gDFC, 2.1 % *trans*-gDFC). MALS-GPC ( $\text{dn dc}^{-1} = 0.1290$ );  $M_N = 96,800$  g mol $^{-1}$ ,  $M_W = 141,000$  g mol $^{-1}$ , PDI = 1.46.

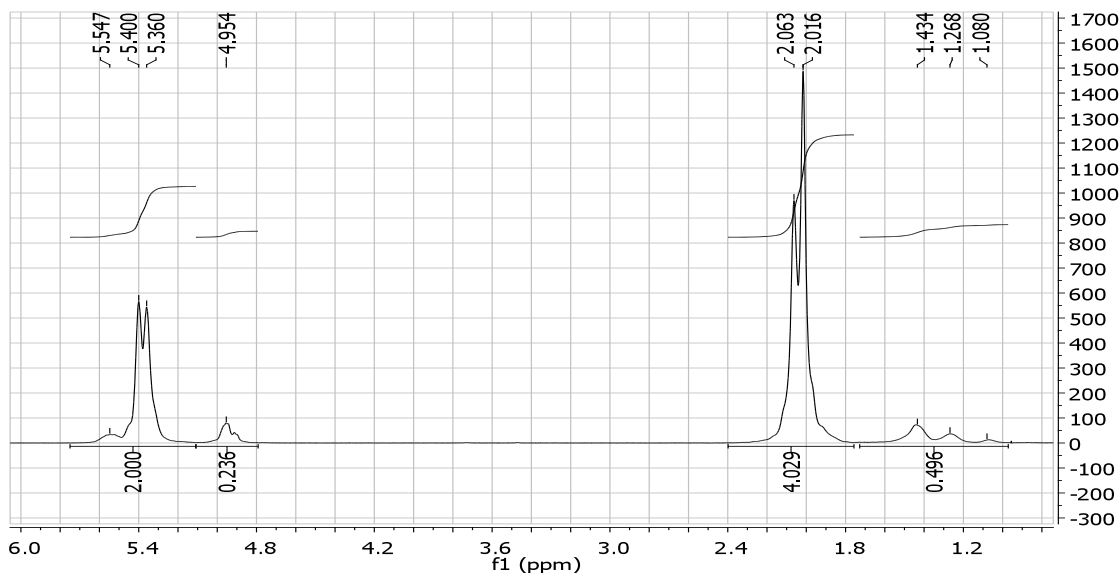


Figure S5:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 97 kDa 3.8 % *c/t*-gDFC-PB.



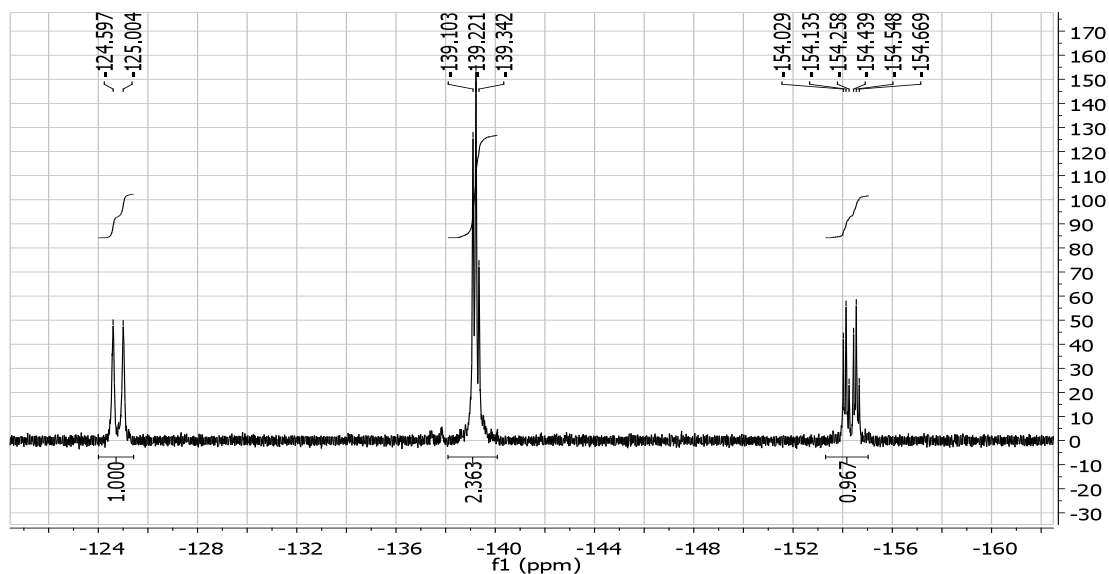


Figure S6:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 97 kDa 3.8 % *c/t*-gDFC-PB.

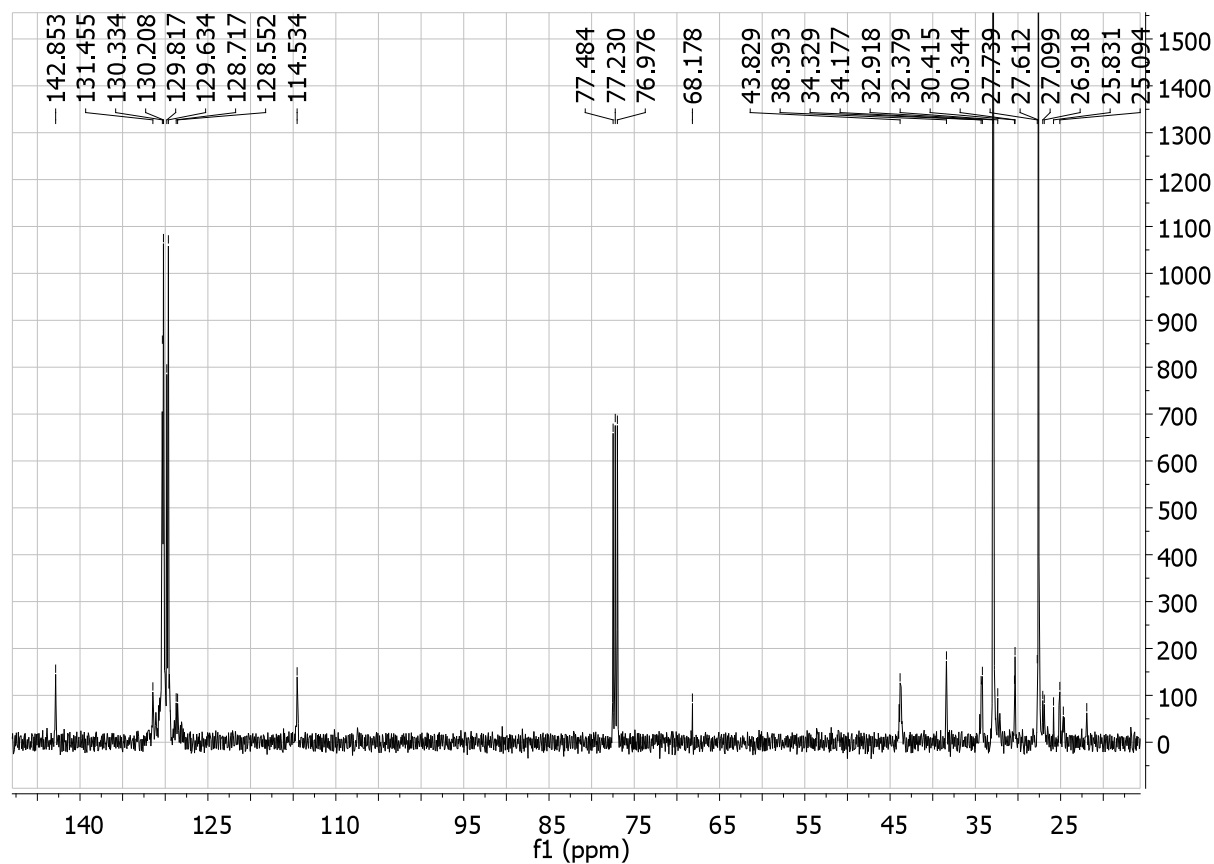


Figure 7:  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) of 97 kDa 3.8 % *c/t*-gDFC-PB.

### 179 kDa 9.1 % *c/t*-gDFC-PB

0.63 g (11.6 mmol) *c/t*-PB was subjected to thermolysis in the presence of sodium chlorodifluoroacetate as described above.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.91 (b, 0.25H), 2.06 (b, 4.00H), 1.27 (b, 0.89H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.8 (d, 2.3F), -139.2 (m, 5.51F), -154.3 (m, 2.18F). Copolymer composition = 80.3 % 1,4-PB; 10.3 % 1,2-PB; 9.1 % gDFC (5.0 % *trans*, 4.1 % *cis*). MALS-GPC ( $\text{dn dc}^{-1} = 0.1135 \text{ mL g}^{-1}$ ),  $M_N = 179,000 \text{ g mol}^{-1}$ ,  $M_W = 294,000 \text{ g mol}^{-1}$ , PDI = 1.64.

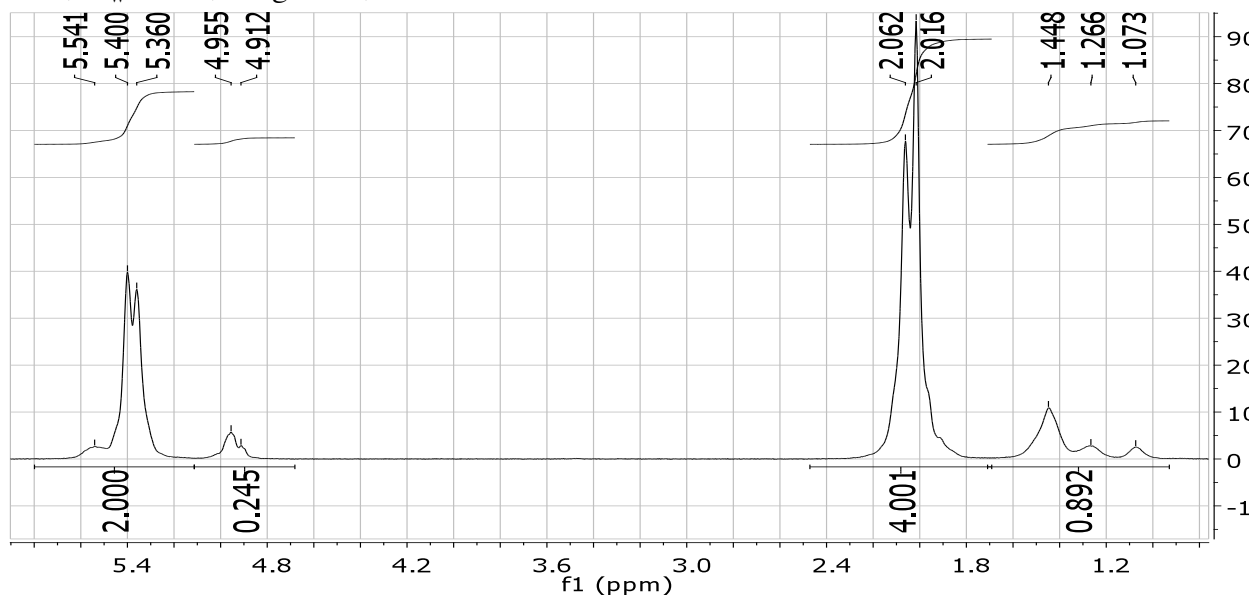


Figure S8:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 9.1 % *c/t*-gDFC-PB.

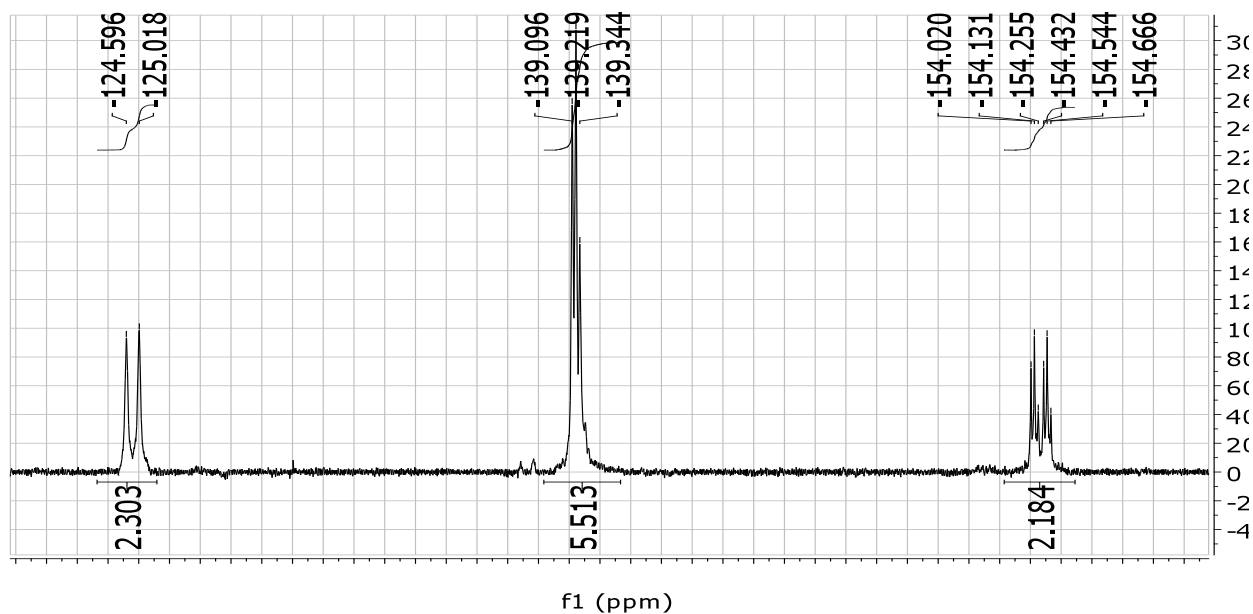


Figure S9:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of 9.1 % *c/t*-gDFC-PB.

### 154 kDa 10.9 % *c/t*-gDFC-PB

0.63 g (11.6 mmol) *c/t*-PB was subjected to functionalization by difluorocarbene by pyrolysis of sodium chlorodifluoroacetate in methyl benzoate.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.95 (m, 0.29H), 2.06 (b, 4.07H), 1.7-1.0 (b, 1.05H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.8 (d, 1F,  $J = 153$  Hz), -139.2 (t, 2.46F,  $J = 45.0$  Hz), -154.3 (dt, 0.91F,  $J = 45.0$  Hz, 155 Hz). Copolymer composition = 79.0 % 1,4-PB; 10.1 % 1,2-PB; 10.9 % gDFC (4.8 % *cis*-gDFC, 6.1 % *trans*-gDFC). MALS-GPC (dn  $\text{dc}^{-1} = 0.1100$ );  $M_N = 154,000$  g  $\text{mol}^{-1}$ ,  $M_W = 236,000$  g  $\text{mol}^{-1}$ , PDI = 1.53.

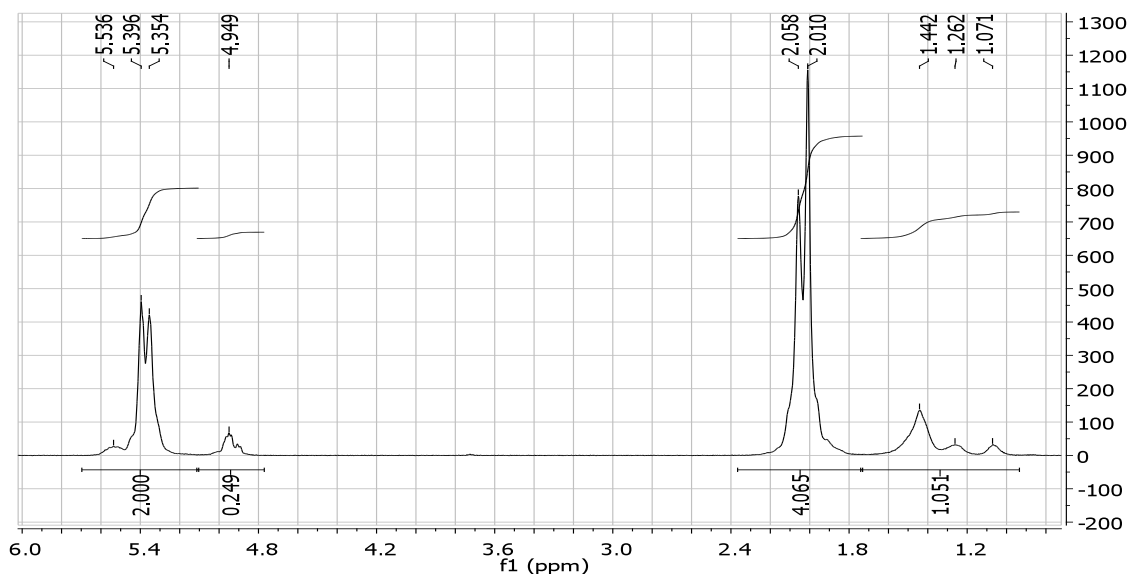


Figure S10:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 154 kDa 10.9 % *c/t*-gDFC-PB.

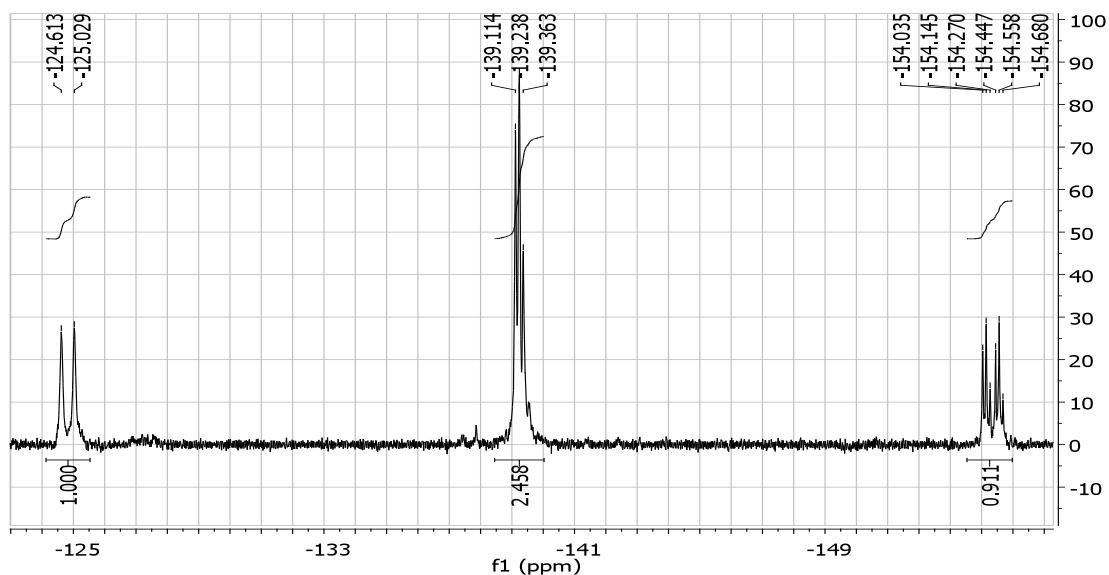


Figure S11:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 154 kDa 10.9 % *c/t*-gDFC-PB.

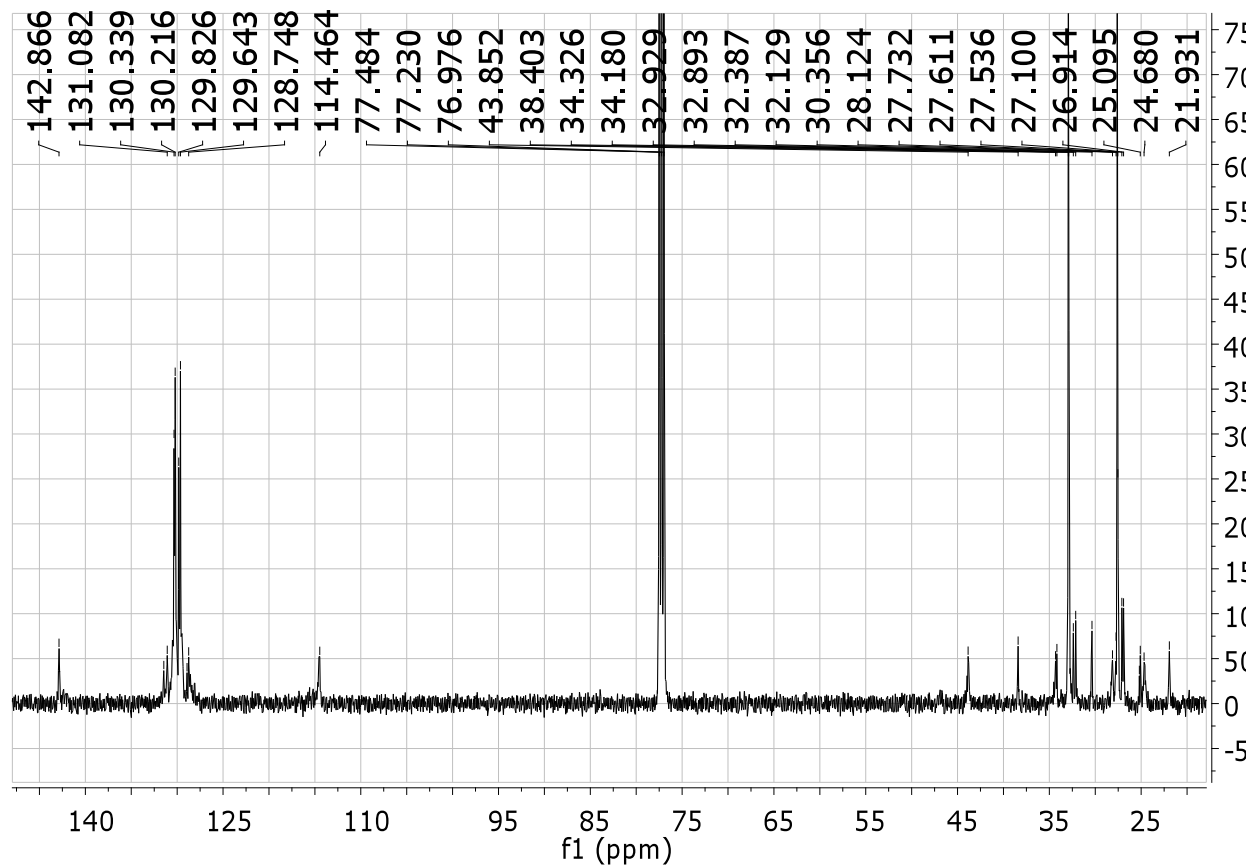


Figure S12:  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) of 154 kDa 10.9 % *c/t*-gDFC-PB.

### 190 kDa 22.0 % *c/t*-gDFC-PB

1.0 g (18.5 mmol) *c/t*-PB was subjected to thermolysis in the presence of sodium chlorodifluoroacetate as described above.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H); 4.96 (b, 0.27H); 2.06 (b, 4.01H); 1.28 (b, 2.12H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) -124.8 (d, 2.23F); -139.2 (m, 5.59F); -154.4 (m, 2.18F). Copolymer composition = 68.3 % 1,4-PB, 9.7 % 1,2-PB, 22.0 % gDFC (9.7 % *cis*, 12.3 % *trans*). MALS-GPC ( $\text{dn dc}^{-1} = 0.0879 \text{ mL g}^{-1}$ );  $M_N = 190,000 \text{ g mol}^{-1}$ ,  $M_W = 282,000 \text{ g mol}^{-1}$ , PDI = 1.49.

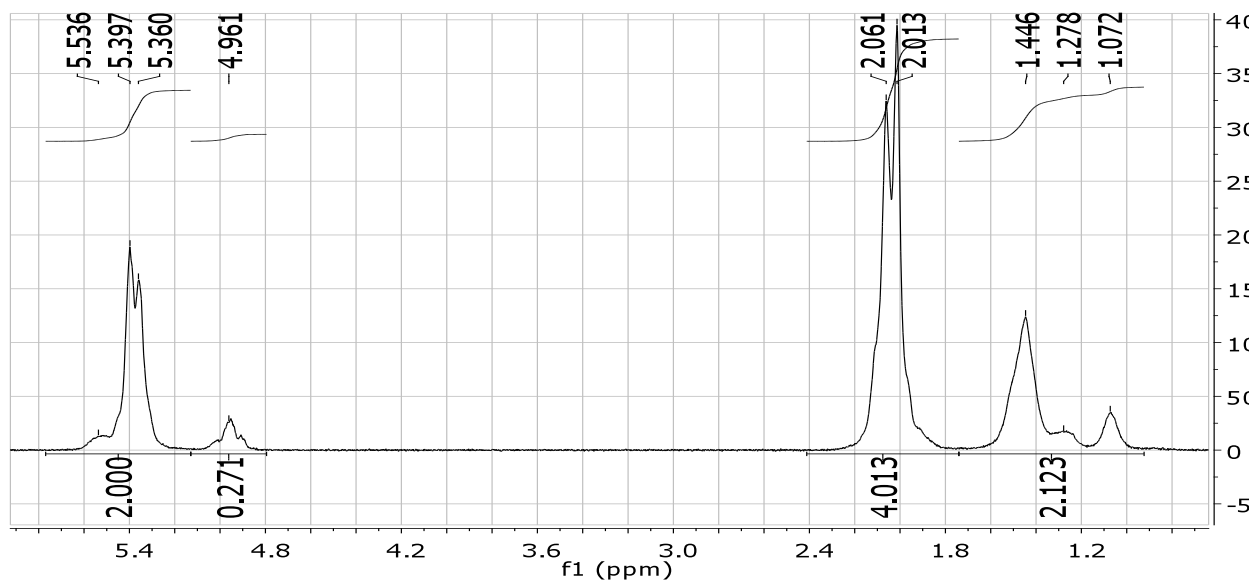


Figure S13:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 22.0 % *c/t*-gDFC-PB.

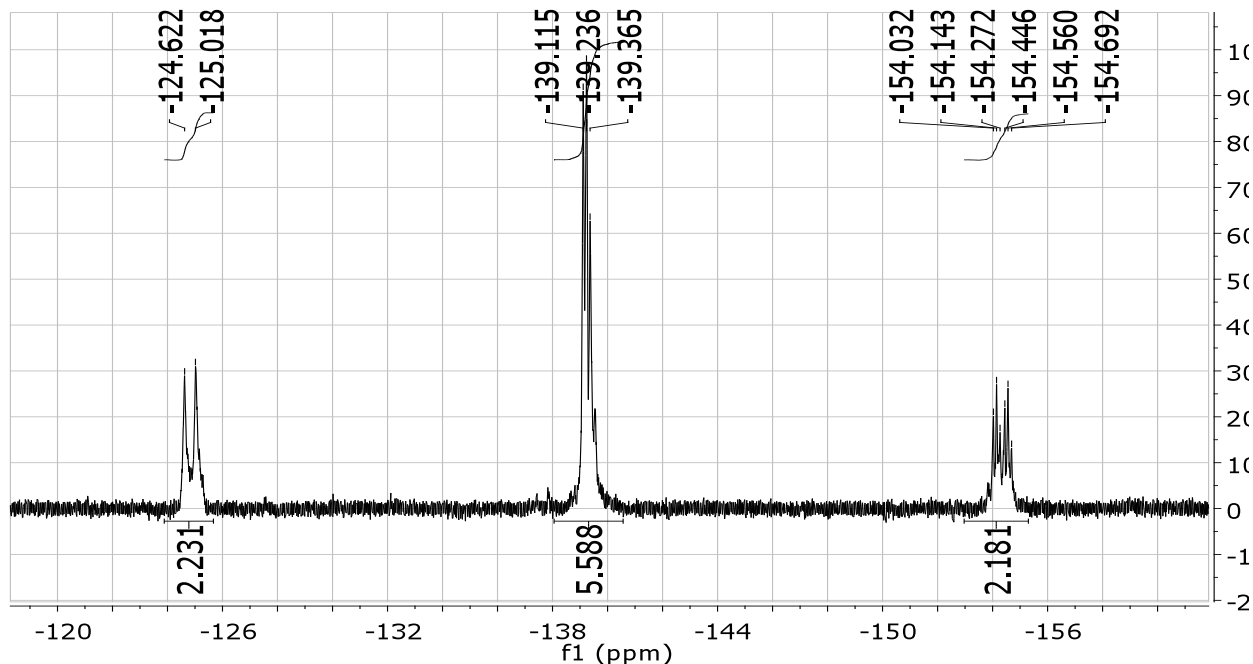


Figure S14:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of 22.0 % *c/t*-gDFC-PB.

### 319 kDa 32.4 % *c/t*-gDFC-PB

0.914 g (16.9 mmol) *c/t*-PB was functionalized with difluorocarbene by pyrolysis of sodium chlorodifluoroacetate in methyl benzoate.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.97 (m, 0.30H), 2.06 (b, 3.89H), 1.7-1.0 (b, 3.42H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.8 (d, 1F,  $J$  = 141 Hz), -139.2 (m, 2.36F), -154.3 (m, 0.95F).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 131.0-128.7, 119.0-114.4, 43.9, 38.3, 34.2, 32.8, 32.3, 32.0, 30.3, 28.1-26.1, 25.1, 24.5, 21.8, 21.4, 19.5, 15.9. Copolymer composition = 58.2 % 1,4-PB; 9.4 % 1,2-PB; 32.4 % gDFC (14.7 % *cis*-gDFC, 17.8 % *trans*-gDFC). MALS-GPC ( $\text{dn dc}^{-1} = 0.0700$ );  $M_N = 319,000 \text{ g mol}^{-1}$ ,  $M_W = 440,000 \text{ g mol}^{-1}$ , PDI = 1.38.

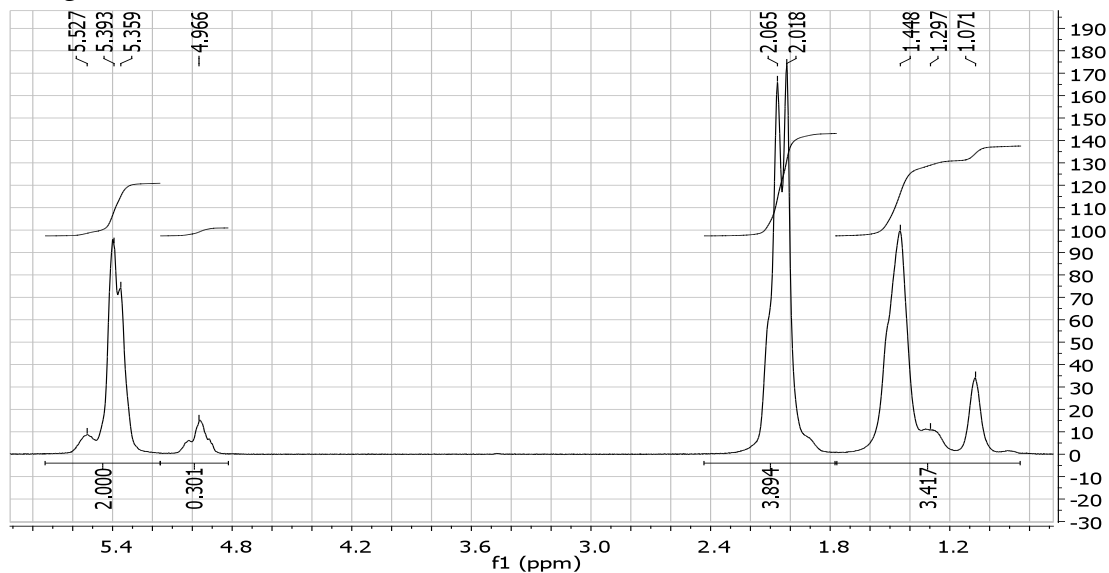


Figure S15:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 319 kDa 32.4 % *c/t*-gDFC-PB.

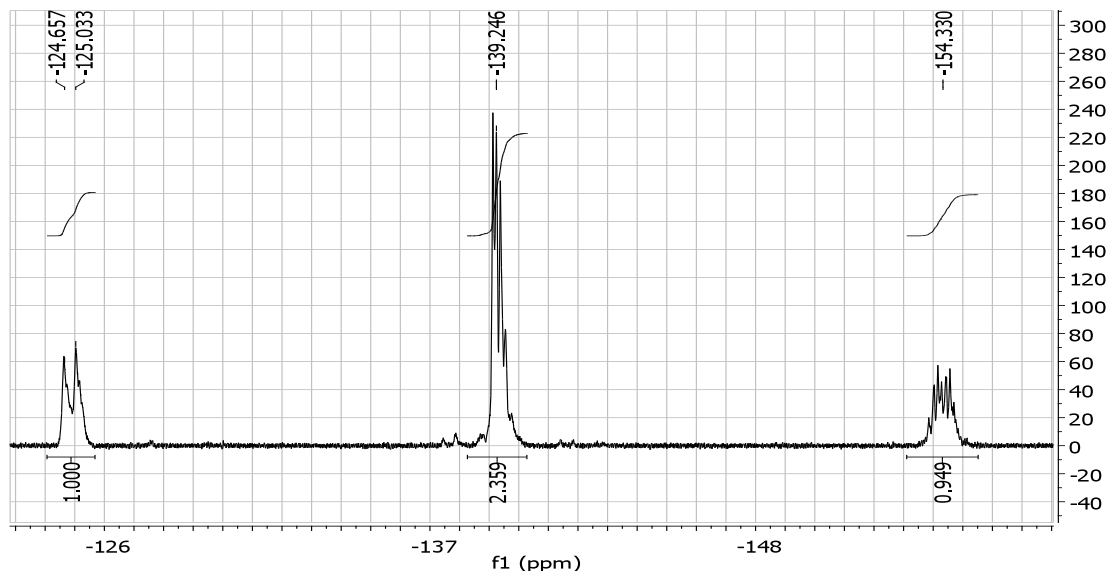


Figure S16:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 319 kDa 32.4 % *c/t*-gDFC-PB.

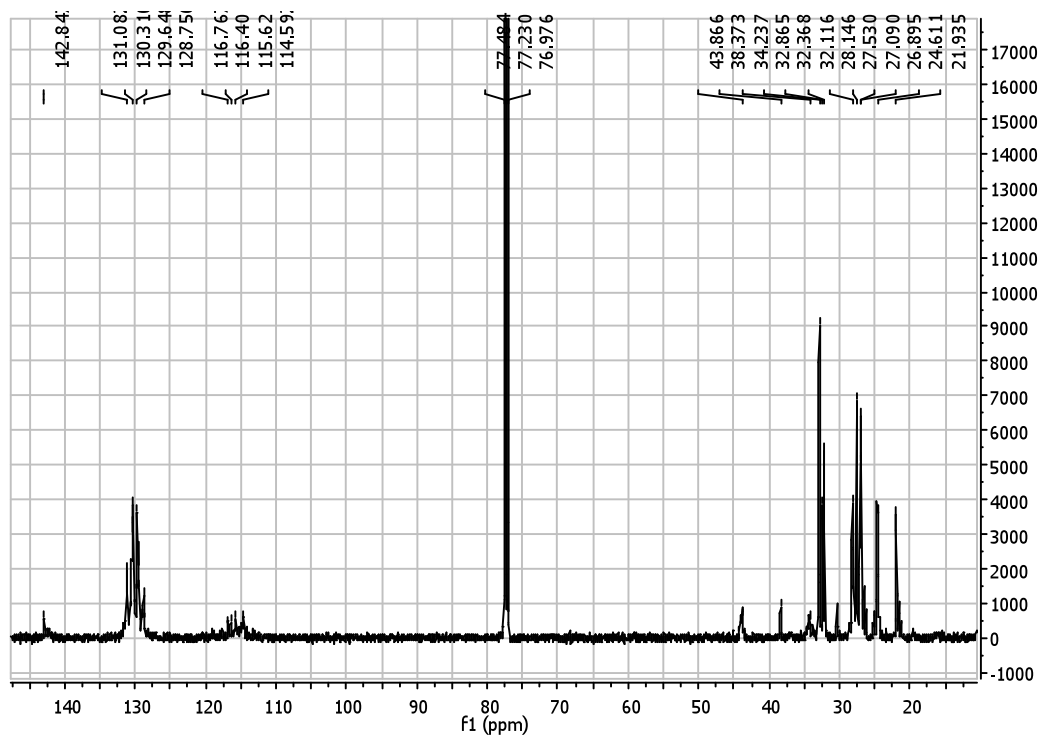


Figure S17:  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) of 319 kDa 32 % *c/t*-gDFC-PB.  $^{13}\text{CF}_2$  resonances at ~116 ppm.

### 275 kDa 36.1 % *c/t*-gDFC-PB

3.0 g (55.5 mmol) *c/t*-PB was functionalized with difluorocarbene by pyrolysis of sodium chlorodifluoroacetate in methyl benzoate.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.96 (m, 0.30H), 2.06 (b, 3.97H), 1.7-1.0 (b, 4.02H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.8 (m, 1F), -139.2 (m, 2.42F), -154.3 (m, 0.91F).  $^{13}\text{C}$  NMR (126 MHz,  $\text{cdCl}_3$ )  $\delta$  132.77, 131.07, 130.75, 130.30, 130.20, 129.65, 129.54, 128.72, 127.93, 118.73, 117.61, 116.44, 116.13, 115.27, 114.17, 112.75, 77.48, 77.23, 76.98, 43.93, 38.43, 32.78, 32.31, 32.08, 29.92, 28.13, 27.96, 27.52, 27.45, 26.98, 26.83, 26.51, 26.22, 24.68, 21.86, 21.48, 21.19, 19.61, 15.98. Copolymer composition = 55.1% 1,4-PB; 8.7 % 1,2-PB; 36.1 % gDFC (16.0 % *cis*-gDFC, 20.1 % *trans*-gDFC). MALS-GPC ( $\text{dn dc}^{-1} = 0.0700$ );  $M_N = 275,000 \text{ g mol}^{-1}$ ,  $M_W = 446,000 \text{ g mol}^{-1}$ , PDI = 1.62.

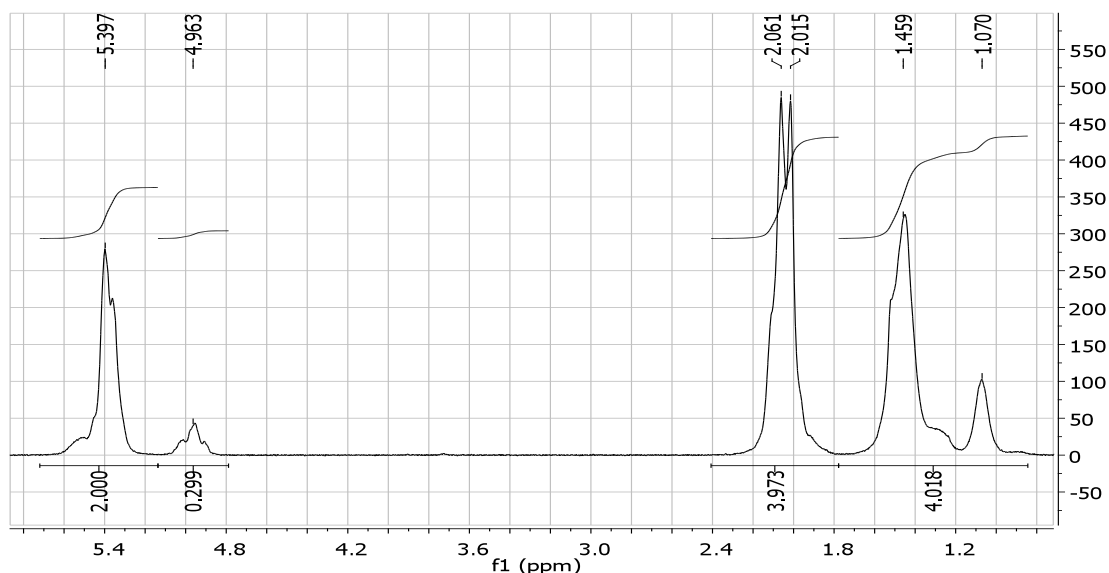


Figure S18:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 275 kDa 36.1 % *c/t*-gDFC-PB.

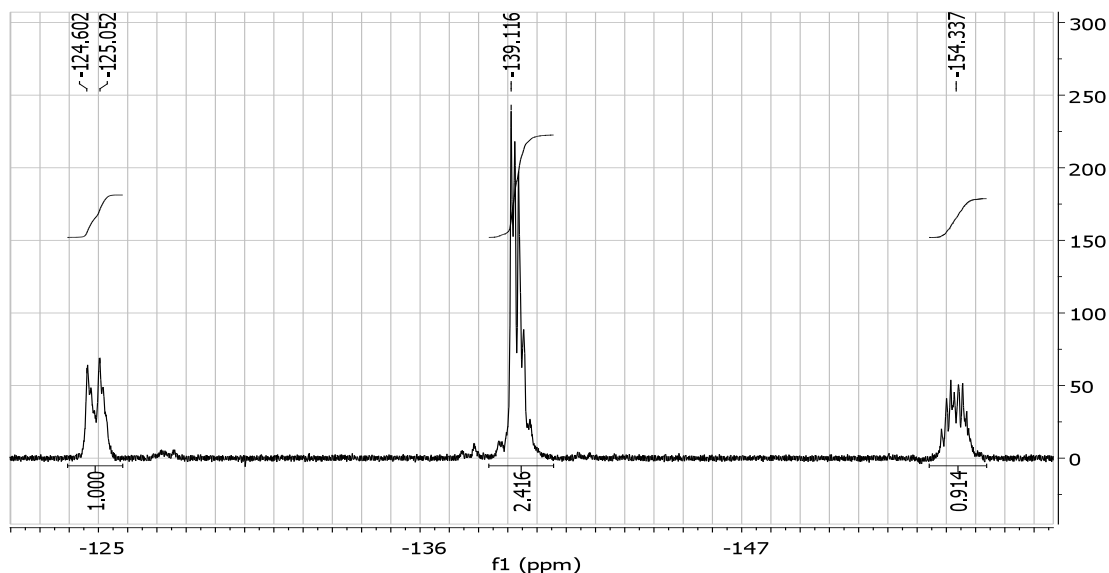


Figure S19:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 275 kDa 36.1 % *c/t*-gDFC-PB.



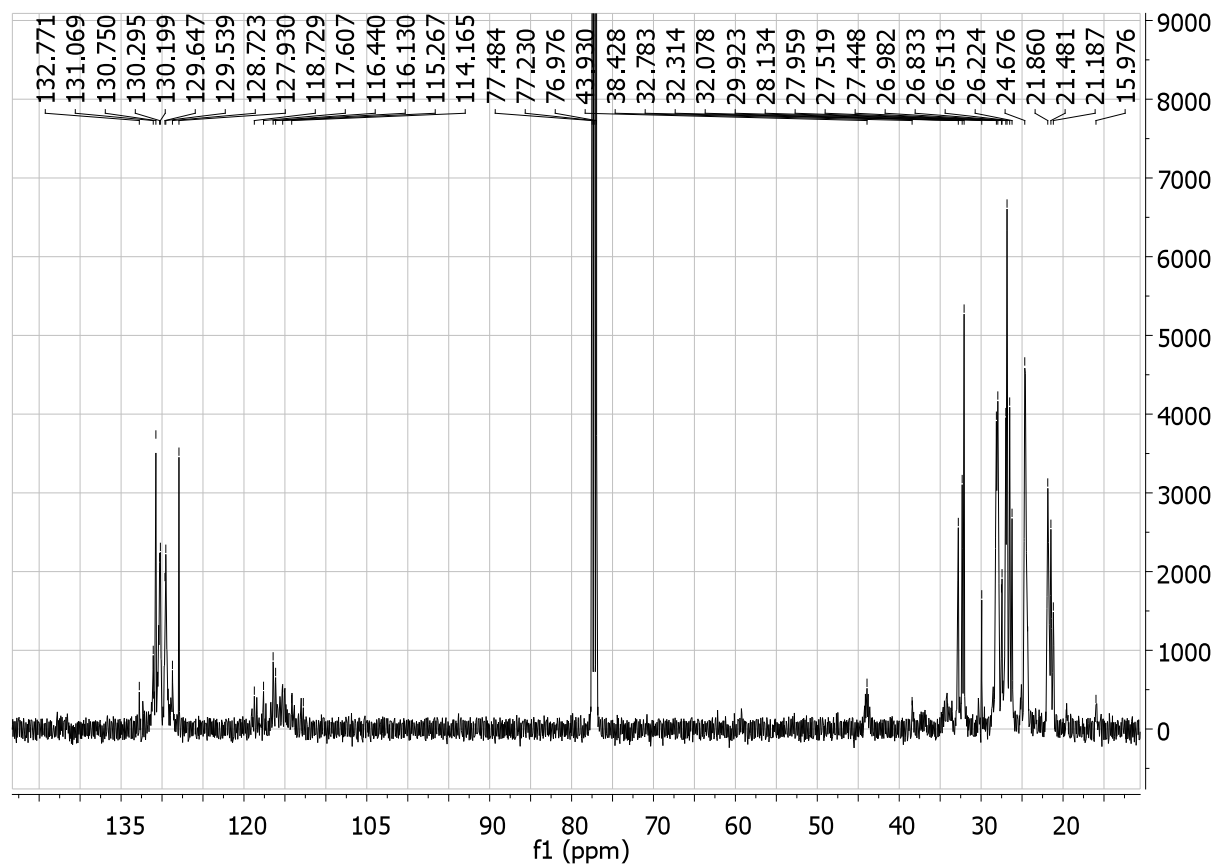


Figure S20:  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) of 275 kDa 36.1 % *c/t*-gDFC-PB.

### 173 kDa 47.4 % *c/t*-gDFC-PB

0.62 g (11.4 mmol) *c/t*-PB was subjected to thermolysis in the presence of sodium chlorodifluoroacetate as described above.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.95 (b, 0.35H), 2.06 (b, 3.97H), 1.28 (b, 6.36H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.0 (m, 2.28F), -139.2 (m, 5.55F), -154.2 (m, 2.17F). Copolymer composition = 44.3 % 1,4-PB, 8.2 % 1,2-PB, 47.4 % gDFC (21.1 % *cis*, 26.3 % *trans*-gDFC). MALS-GPC ( $\text{dn dc}^{-1} = 0.0613 \text{ mL g}^{-1}$ ),  $M_N = 173,000 \text{ g mol}^{-1}$ ,  $M_W = 279,000 \text{ g mol}^{-1}$ , PDI = 1.61.

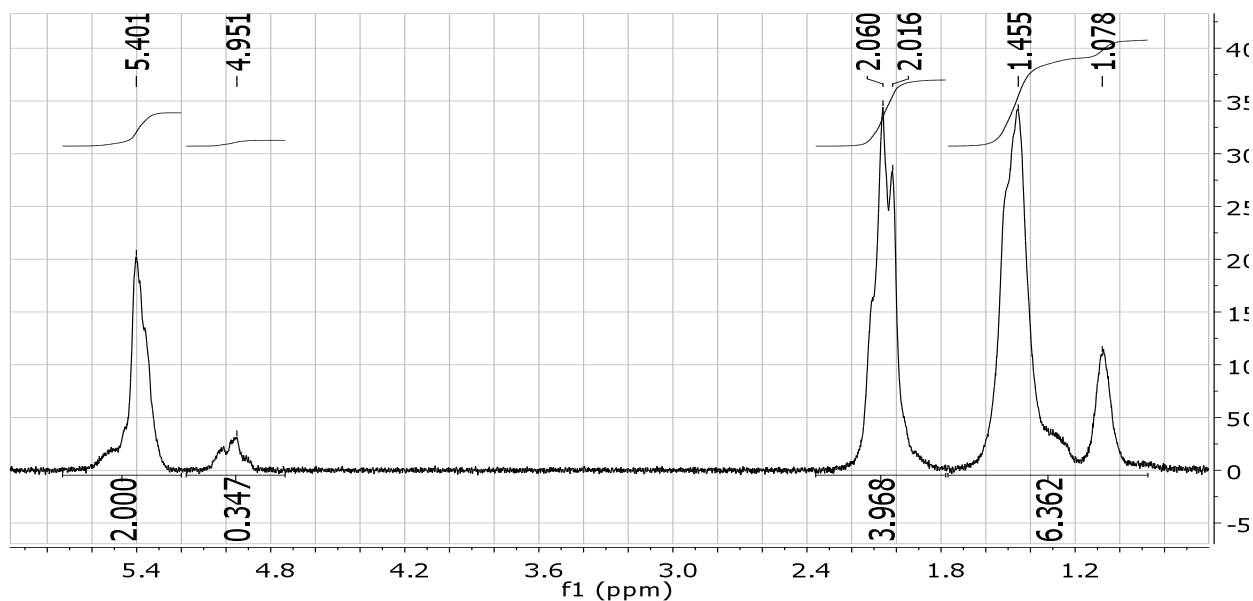


Figure S21:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 47.4 % *c/t*-gDFC-PB.

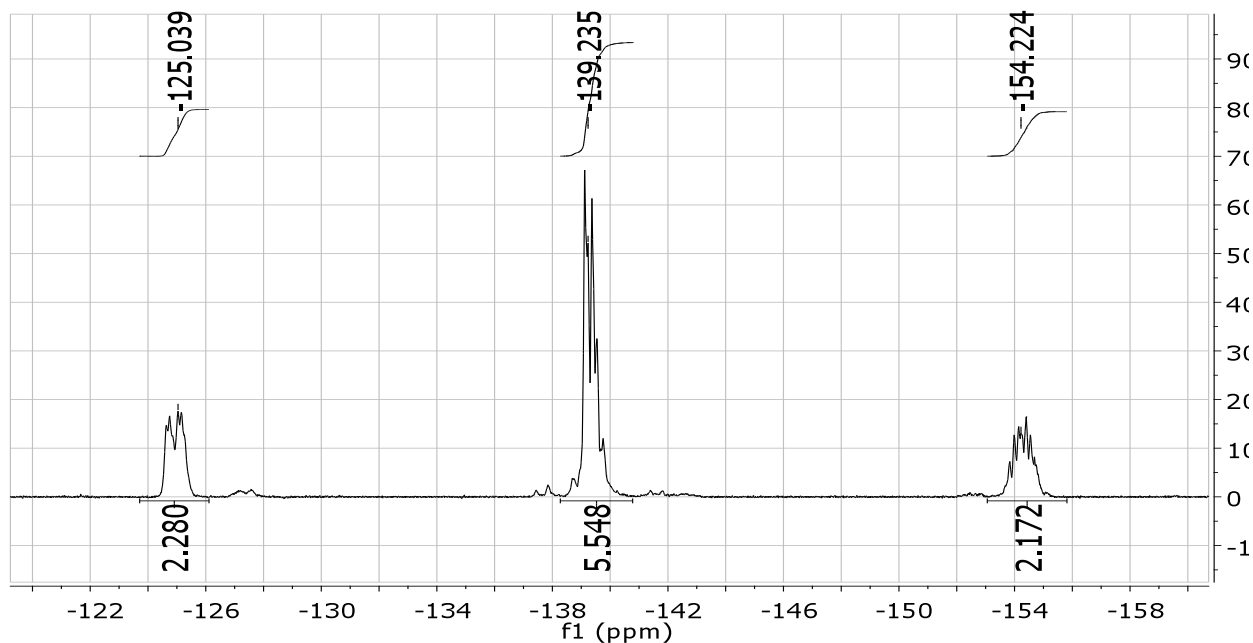


Figure S22:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of 47.3 % *c/t*-gDFC-PB.

### 290 kDa 51.7 % *c/t*-gDFC-PB

0.815 g (15.7 mmol) *c/t*-PB was subjected to functionalization by difluorocarbene by pyrolysis of sodium chlorodifluoroacetate in methyl benzoate.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.98 (m, 0.38H), 2.06 (b, 3.98H), 1.7-1.0 (b, 7.60H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.0 (m, 1F), -139.4 (m, 2.47F), -154.3 (m, 0.96F).  $^{13}\text{C}$  NMR  $\delta$  142.52, 142.33, 130.37, 129.94, 129.71, 118.70, 117.58, 116.70, 116.41, 116.11, 115.30, 115.06, 114.32, 114.09, 113.27, 113.01, 77.48, 77.23, 76.98, 44.00, 34.23, 32.80, 32.30, 32.08, 31.89, 28.33, 27.60, 27.52, 27.04, 26.58, 25.63, 24.77, 21.94, 21.54. Copolymer composition = 40.1% 1,4-PB; 8.2 % 1,2-PB; 51.7 % gDFC (22.9 % *cis*-gDFC, 28.8 % *trans*-gDFC). MALS-GPC ( $\text{dn dc}^{-1} = 0.0580$ );  $M_N = 290,000 \text{ g mol}^{-1}$ ,  $M_W = 400,000 \text{ g mol}^{-1}$ , PDI = 1.38.

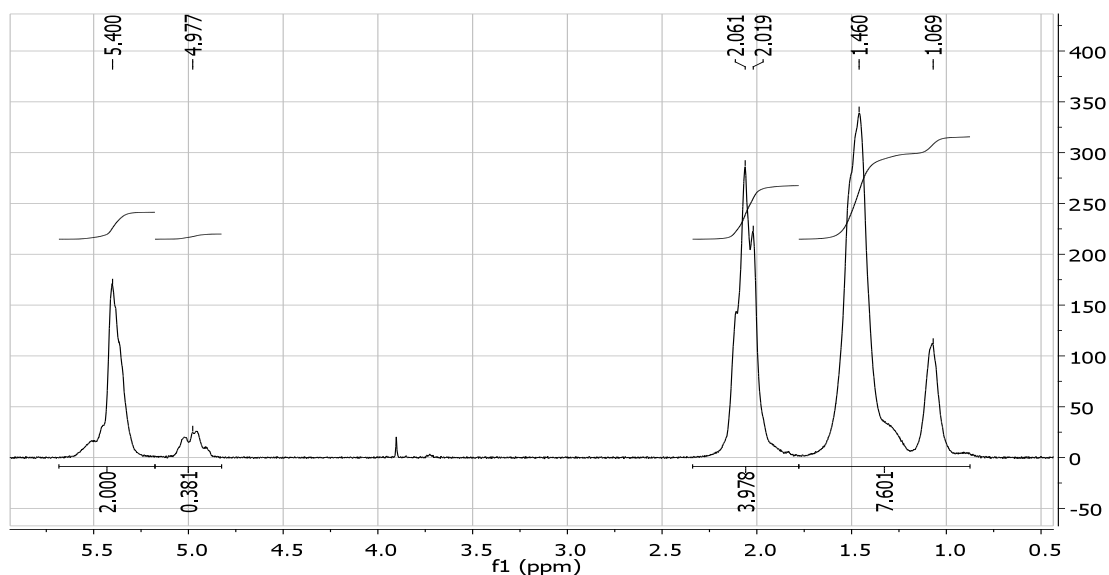


Figure S23:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 290 kDa 51.7 % *c/t*-gDFC-PB.

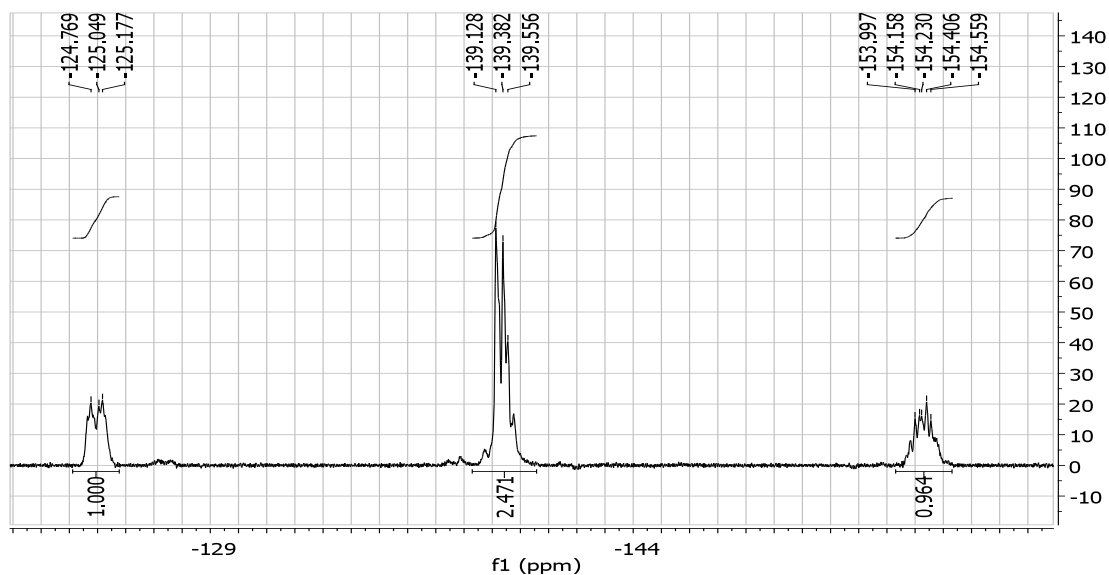


Figure S24:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 290 kDa 51.7 % *c/t*-gDFC-PB.

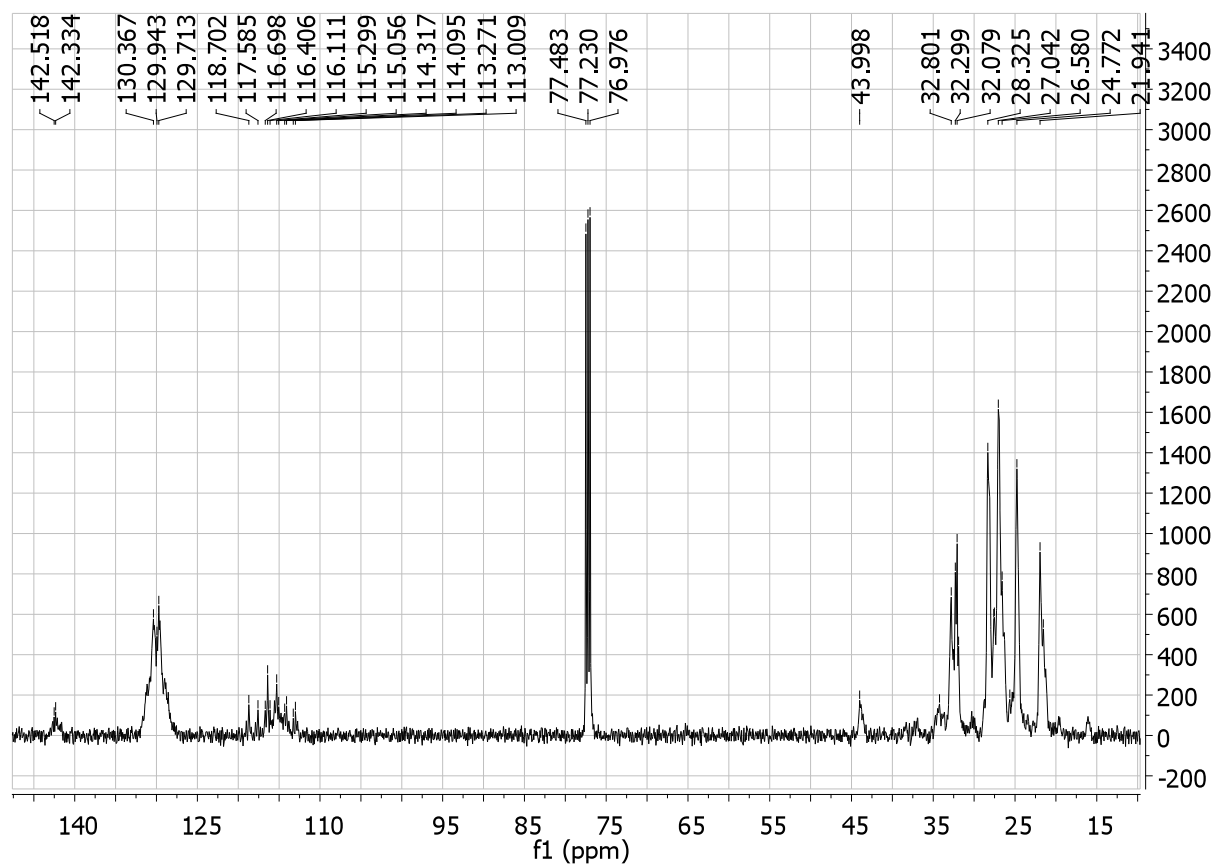


Figure S25: <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) of 290 kDa 51.7 % *c/t*-gDFC-PB.

### 88.4 kDa 58.7 % *c/t*-gDFC-PB

0.100 g (1.85 mmoles) *c/t*-PB was subjected to functionalization by difluorocarbene by pyrolysis of sodium chlorodifluoroacetate in methyl benzoate.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (b, 2.00H), 4.96 (m, 0.38H), 2.07 (b, 4.07H), 1.7-1.0 (b, 9.97H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.0 (m, 1F), -139.4 (m, 2.36F), -154.3 (m, 0.90F).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.42, 141.87, 131.11, 130.34, 130.25, 129.68, 129.58, 128.78, 118.71, 117.59, 116.72, 116.41, 116.13, 115.57, 115.28, 115.00, 114.42, 114.12, 113.85, 112.99, 77.48, 77.23, 76.98, 43.97, 38.38, 36.87, 34.28, 32.83, 32.33, 32.08, 30.33, 28.26, 28.08, 27.56, 26.88, 26.57, 26.28, 24.73, 23.46, 21.91, 21.53, 19.47, 16.04. Copolymer composition = 34.2% 1,4-PB; 7.1 % 1,2-PB; 58.7 % gDFC (26.2 % *cis*-gDFC, 32.5 % *trans*-gDFC). MALS-GPC (dn  $\text{dc}^{-1} = 0.0551$ );  $M_N = 88,400 \text{ g mol}^{-1}$ ,  $M_W = 148,000 \text{ g mol}^{-1}$ , PDI = 1.68.

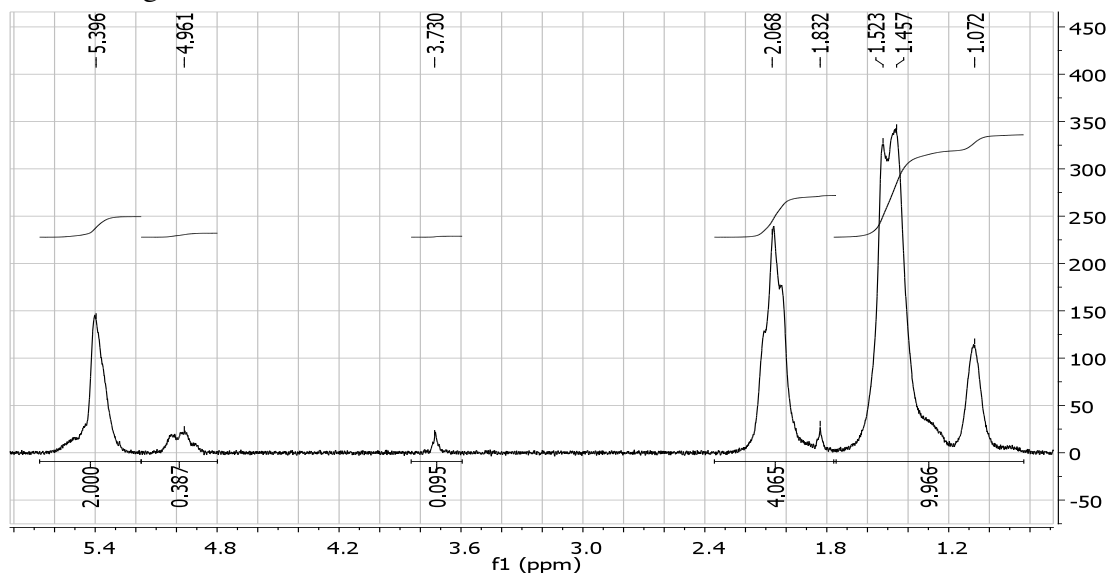


Figure S26:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 88 kDa 58.7 % *c/t*-gDFC-PB. Residual THF resonances are observed at 3.73 and 1.83 ppm.

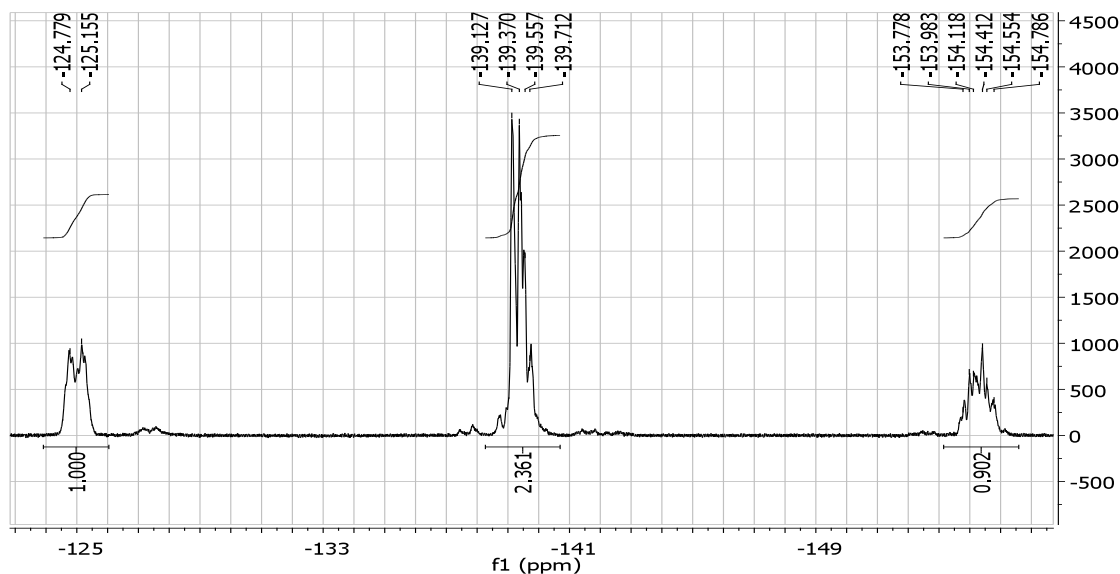


Figure S27:  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ) of 88 kDa 58.7 % *c/t*-gDFC-PB.

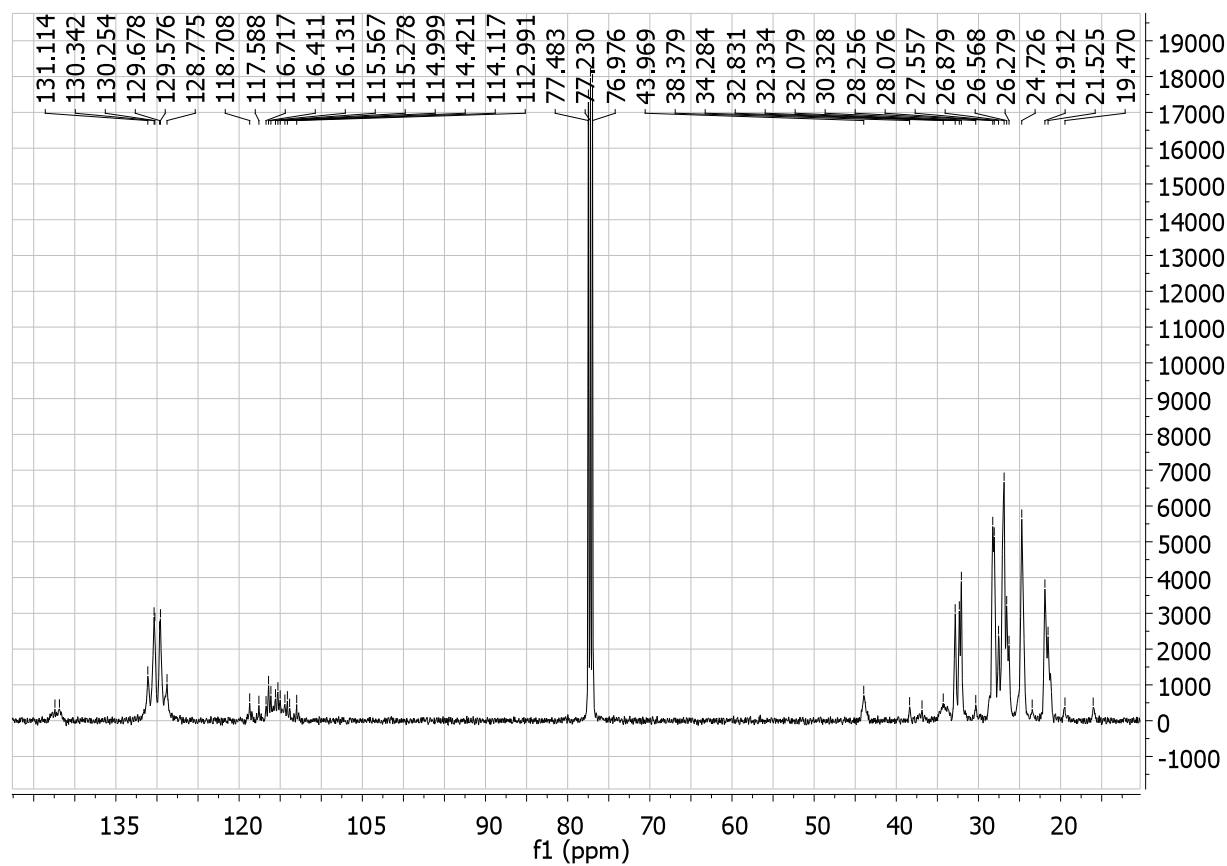


Figure S28:  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ) of 88 kDa 58.7 % *c/t*-gDFC-PB.  $^{13}\text{CF}_2$  resonances ~116 ppm.

### 177 kDa 95.1 % *c/t*-gDFC-PB

0.262 g (4.8 mmol) *c/t*-PB was subjected to thermolysis in the presence of sodium chlorodifluoroacetate as described above.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.41 (b, 2.00H), 5.04 (b, 1.81H), 2.07 (b, 3.63H), 1.4 (b, 182.9H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.2 (m, 2.23F), -139.5 (m, 5.69F), -154.0 (m, 2.08F). Copolymer composition = 2.0 % 1,4-PB, 2.9 % 1,2-PB, 95.1 % gDFC (41.0 % *cis*-, 54.1 % *trans*). MALS-GPC ( $\text{dn dc}^{-1} = 0.0440 \text{ mL g}^{-1}$ ),  $M_N = 177,000 \text{ g mol}^{-1}$ ,  $M_W = 258,000 \text{ g mol}^{-1}$ , PDI = 1.45.

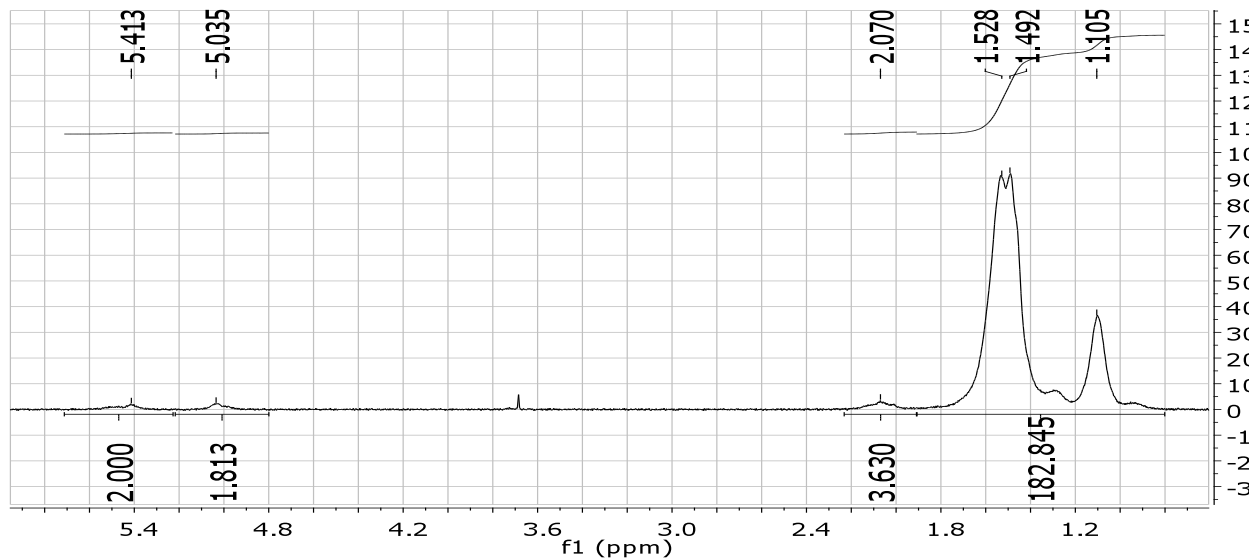


Figure S29:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 95.1 % *c/t*-gDFC-PB.

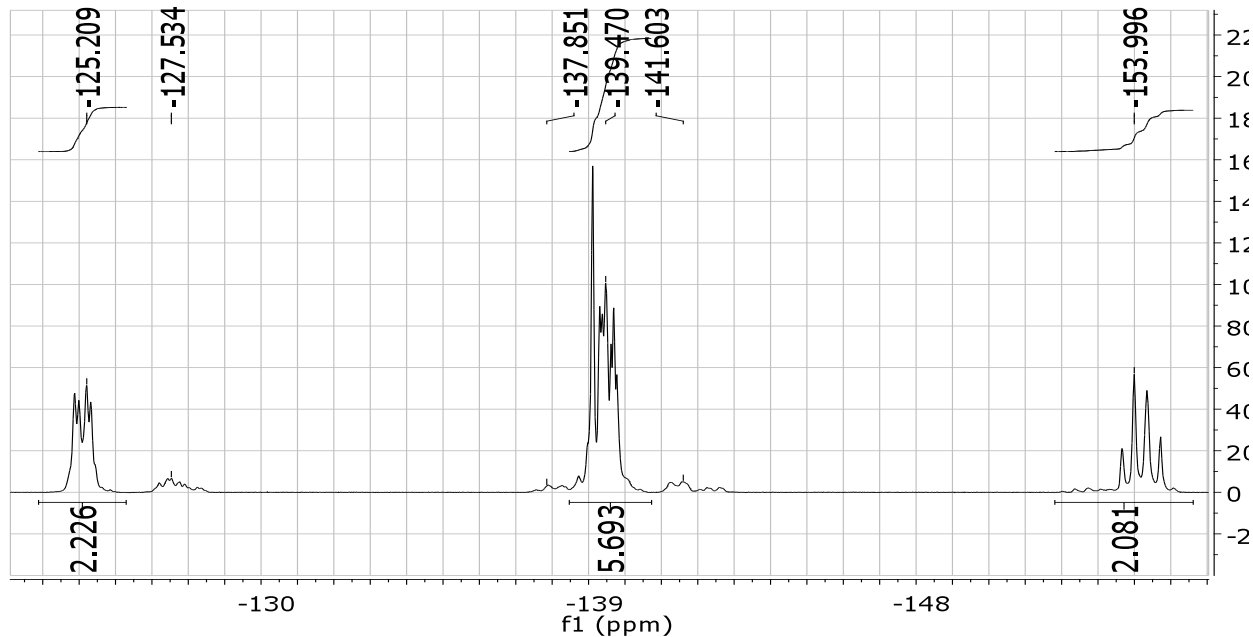
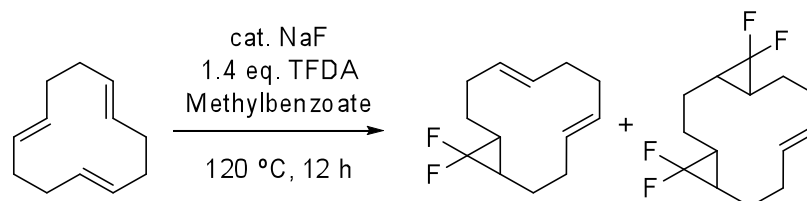


Figure S30:  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) of 95.1 % *c/t*-gDFC-PB.

**(4Z,8Z)-13,13-Difluoro-bicyclo[10.1.0]trideca-4,8-diene and (9E)-5,5,14,14-tetrafluoro-tricyclo[11.1.0.0<sup>4,6</sup>]tetradec-9-ene**



A Teflon-coated magnetic stirrer was added to a recently flame-dried and vacuum-cooled 250 mL three-neck flask under a dinitrogen atmosphere with oven-dried sodium fluoride (30 mg, 0.71 mmol). The flask was charged via cannula with a stock solution of 1,3,5-cyclododecatriene (4.5 g, 27.7 mmol) in methyl benzoate (1.9 g, 14 mmol). An oven-dried syringe was charged with TFDA (9.77 g, 39.1 mmol), attached to a syringe pump, and fitted to the three-neck flask. After heating the three-neck flask to 120 °C (external temperature, oil bath), the syringe pump was turned on and allowed to pump at a rate of 1.0 mL per hour. After complete addition, the reaction was allowed to stir for an additional 5 h, and allowed to cool to ambient temperature. Isolation of both products was accomplished by careful column chromatography of the entire reaction using hexane as eluant: 3.464 g of bis-addition product (47.7 % isolated yield, Rf 0.3) and 1.566 g of mono-addition product (26.6 % isolated yield, Rf 0.6). The reaction using pyrolysis of sodium chlorodifluoroacetate also gave both products, but in appreciably lower yields (13.8 and 4.2 %, respectively, from 2.0 eq. difluoroacetate at 190 °C).

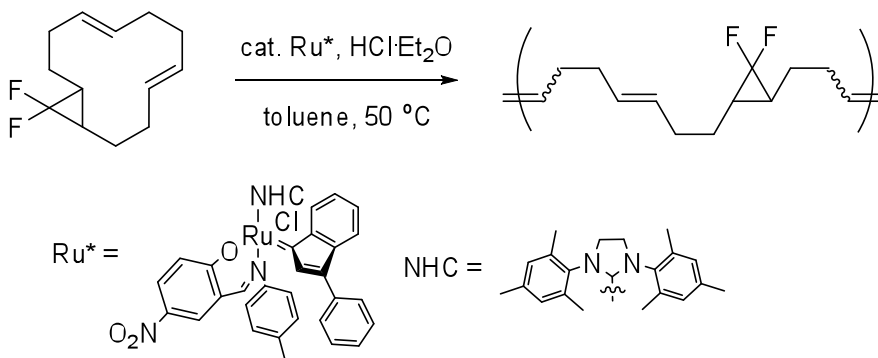
(4Z,8Z)-13,13-Difluoro-bicyclo[10.1.0]trideca-4,8-diene (mono-addition product): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.19 (s, 2H, olefin), 2.40-2.10 (m, 4H, allylic), 2.08-1.85 (m, 6H, allylic & homoallylic), 1.10 (s, 2H, homoallylic), 0.95 (q, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>H-F</sub> = 7.2 Hz, 2H, cyclopropyl). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 132.24, 129.79, 115.13 (t, *J* = 279 Hz, CF<sub>2</sub>), 31.86, 31.18, 28.22, 26.46. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -139.62 (t, 2F, *J*<sub>F-H</sub> = 7.2 Hz).

(9E)-5,5,14,14-tetrafluoro-tricyclo[11.1.0.0<sup>4,6</sup>]tetradec-9-ene (bis-addition product, 1.0 : 3.3 mixture of two regioisomers from integration of the <sup>19</sup>F and <sup>13</sup>C NMR): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.46 (m, 2H, olefinic), 2.25-1.65 (m, 8H, allylic & homo-cyclopropyl), 1.45-1.15 (m, 6H, homo-cyclopropyl & cyclopropyl), 1.14-0.85 (m, 2H, cyclopropyl). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) (minor isomer peaks denoted with \*) δ 131.15, 130.71\*, 115.80\* (t, *J*<sub>C-F</sub> = 288.1 Hz, cyclopropyl CF<sub>2</sub>), 115.25 (t, *J*<sub>C-F</sub> = 287.7 Hz, cyclopropyl CF<sub>2</sub>), 31.4, 30.77\*, 20.02 (t, *J*<sub>C-CF</sub> = 8.8 Hz, cyclopropyl CHCF<sub>2</sub>), 27.2\* (t, *J*<sub>C-CF</sub> = 8.5 Hz, cyclopropyl CHCF<sub>2</sub>), 26.99 (t, *J*<sub>C-CF</sub> = 9.0 Hz, cyclopropyl CHCF<sub>2</sub>), 24.6, 23.98\*, 23.73. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Isomer I: δ -137.35\* (dd, 2F, *J*<sub>F-F</sub> = 153.7 Hz, *J*<sub>CF-C</sub> = 15.3 Hz), -139.92\* (dd, 2F, *J*<sub>F-F</sub> = 153.7 Hz, *J*<sub>CF-C</sub> = 15.3 Hz); Isomer II: δ -138.95 (dd, 2F, *J*<sub>F-F</sub> = 154.2 Hz, *J*<sub>CF-C</sub> = 14.7 Hz), -140.1 (dd, 2 F, *J*<sub>F-F</sub> = 154.2 Hz, *J*<sub>CF-C</sub> = 14.9 Hz).

Both products were found to be unstable under all conditions attempted for MS analysis, but elemental analysis generated satisfactory results. Mono-addition product: Calculated C, 73.55; H, 8.55; F, 17.90; Found C, 73.41; H, 8.52; F, 17.68. Bis-addition product: C, 64.11; H, 6.92; F, 28.97; Found C, 63.96; H, 6.85; F, 28.79.



### 65.5 kDa 33.3 % *trans*-gDFC-PB [ROMP]



To a flame-dried and vacuum-cooled 20 mL round bottom flask equipped with a reflux condenser under an atmosphere of dinitrogen was added (4Z,8Z)-13,13-Difluorobicyclo[10.1.0]trideca-4,8-diene (500 mg, 2.35 mmol), toluene (2.6 mL, 1.1 M), Ru\* (2.22 mg, 2.5  $\mu\text{mol}$ ), and 2.5  $\mu\text{L}$  of a 1.0 M solution of hydrochloric acid in diethyl ether. The flask was reequipped with the reflux condenser, allowed to stir for 2 minutes, then lowered into an oil bath already heated to 50  $^\circ\text{C}$ . After 3.5 hours, the flask was removed, allowed to cool to ambient temperature, and 20 mL of methanol was added to precipitate a light tan solid. This was decanted, redissolved in 5 mL of chloroform, reconcentrated under reduced pressure to about 1.0 mL of volume, and another 20 mL of methanol was added to reprecipitate the polymer. This was repeated three times, then the polymer was dried under vacuum (20 mm Hg) overnight to yield 452 mg of the title compound as a light tan elastic solid (90 % isolated yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.38 (b, 4.00H), 2.02 (b, 8.00H), 1.7-0.8 (b, 3.45H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -139.20 (d, 1F,  $J$  = 50.1 Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 131.0, 130.2, 129.5, 116.7 (t,  $J$  = 286 Hz,  $\text{CF}_2$ ), 32.8, 32.1, 28.1, 27.5, 27.1, 26.9. Olefin to gDFC composition = 67.7 % olefin to 33.3 % gDFC with no discernable other functional groups present. MALS-GPC (dn  $\text{dc}^{-1}$  = 0.0650  $\text{mL g}^{-1}$ );  $M_N$  = 65,500  $\text{g mol}^{-1}$ ,  $M_W$  = 95,200  $\text{g mol}^{-1}$ , PDI = 1.45.

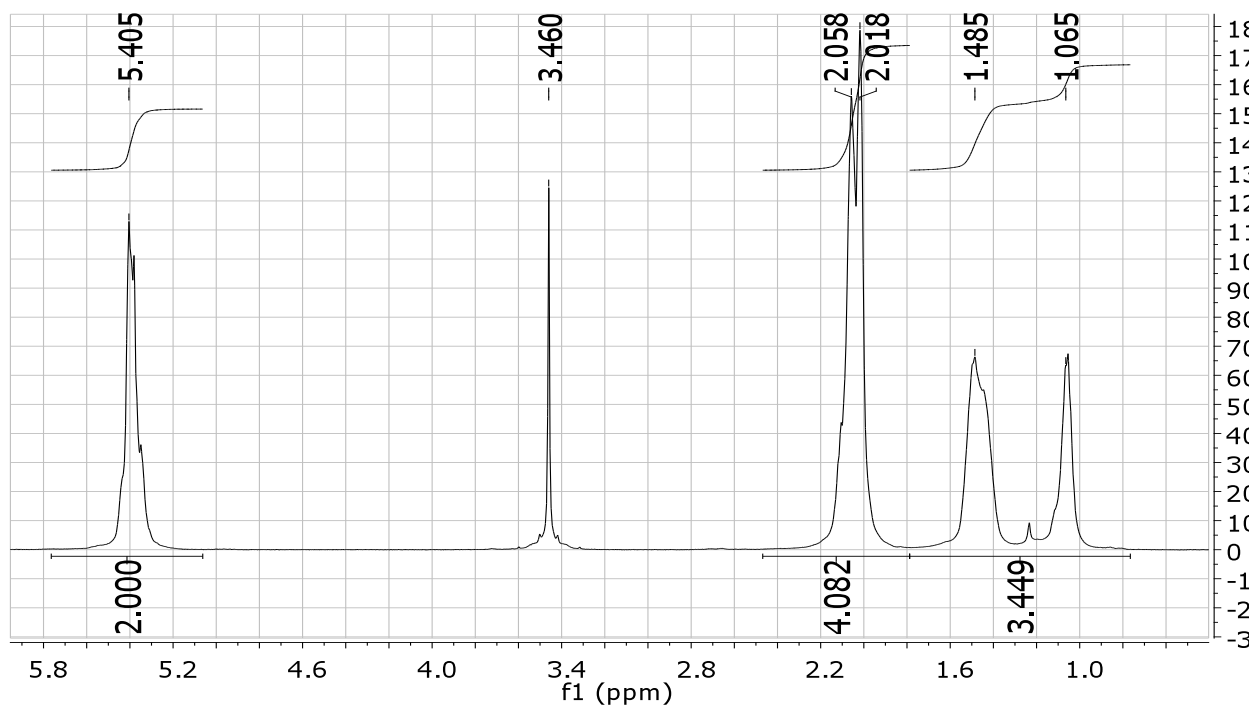


Figure S31: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 33.3 % *trans*-gDFC-PB. Residual methanol at 3.46 ppm.

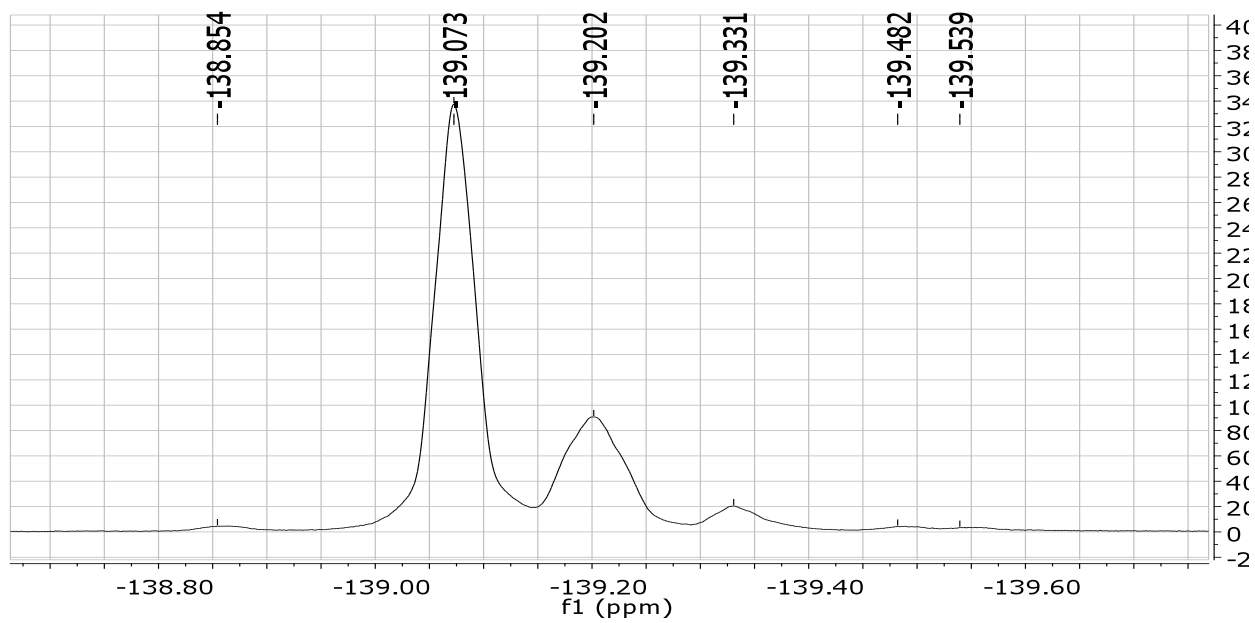


Figure S32: <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) of 33.3 % *trans*-gDFC-PB.

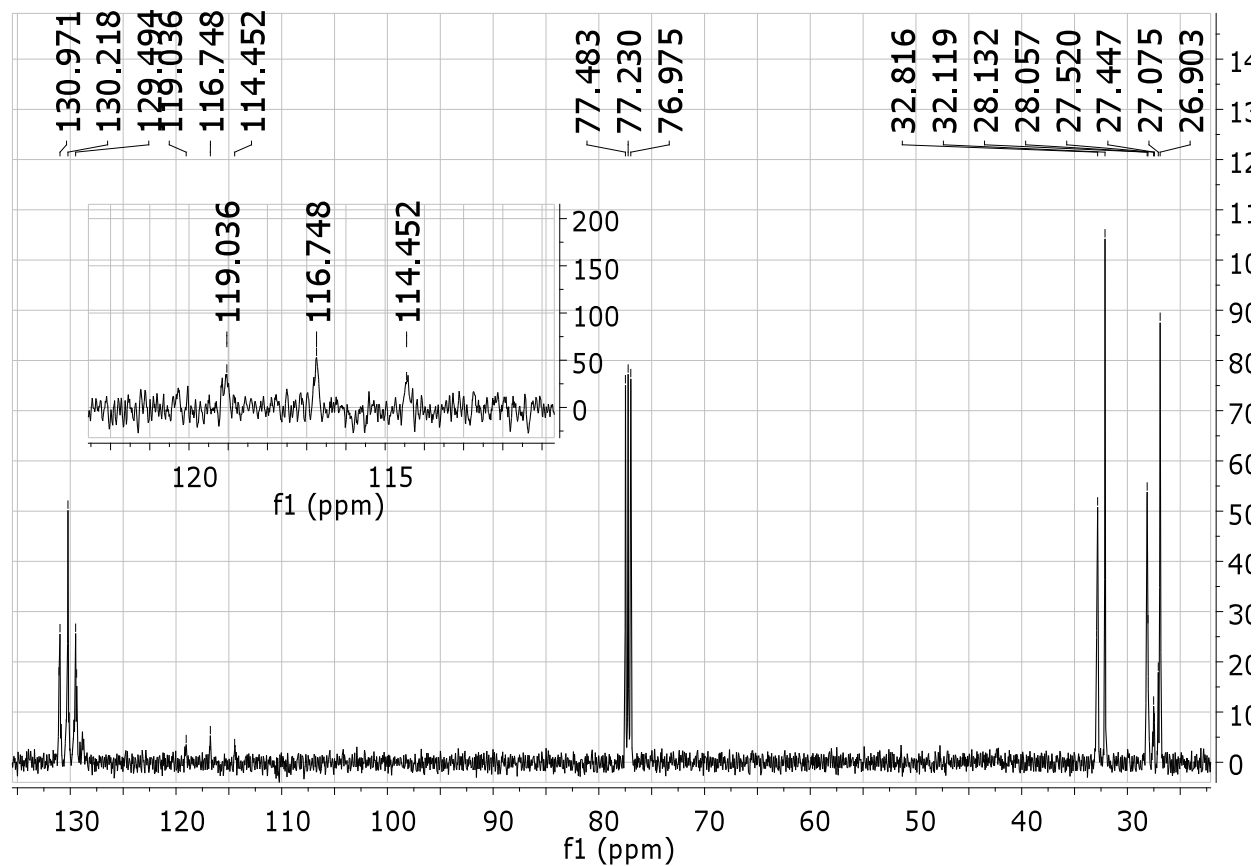
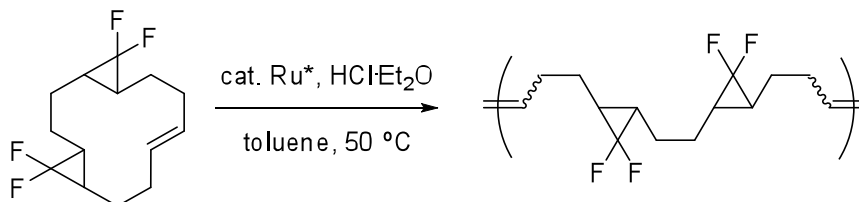


Figure S33:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of 33.3 % *trans*-gDFC-PB,  $^{13}\text{CF}_2$  resonances at ~116 ppm.

## 66.2 kDa 66.7 % *trans*-bis-gDFC-PB [ROMP]



The reaction was carried out exactly as above, using (9E)-5,5,14,14-tetrachloro-tricyclo[11.1.0.0<sup>4,6</sup>]tetradec-9-ene in place of the mono-addition monomer, with slightly different quantities of reagents. Monomer (600 mg, 2.2 mmol), 1.1 mL of toluene, Ru\* (1.1 mg, 1.21  $\mu$ mol), and 1.21  $\mu$ L of 1.0 M hydrochloric acid in diethyl ether were reacted as above. The reaction was stirred at 50 °C for 12 hours, and worked up similarly as above to give 282 mg of a light tan solid (47 % isolated yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.41 (b, 2.00H), 2.07 (b, 4.17H), 1.51 (b, 8.27H), 1.08 (b, 3.98H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -138.7, -139.1 (d, 1F, *J* = 21.8 Hz), -138.4 (d, 1F, *J* = 58.7 Hz), -138.5, -139.8. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 130.2, 129.6, 116.5 (t, *J* = 288.5 Hz, CF<sub>2</sub>), 32.1, 28.2 (m, *syn* and *anti* isomers), 27.0, 26.8, 26.6, 26.2. Olefin to gDFC composition = 33.3 % olefin to 67.7 % gDFC with no discernable other functional groups present. MALS-GPC (dn dc<sup>-1</sup> = 0.0400 mL g<sup>-1</sup>); *M<sub>N</sub>* = 66,200 g mol<sup>-1</sup>, *M<sub>w</sub>* = 112,000 g mol<sup>-1</sup>, PDI = 1.69.

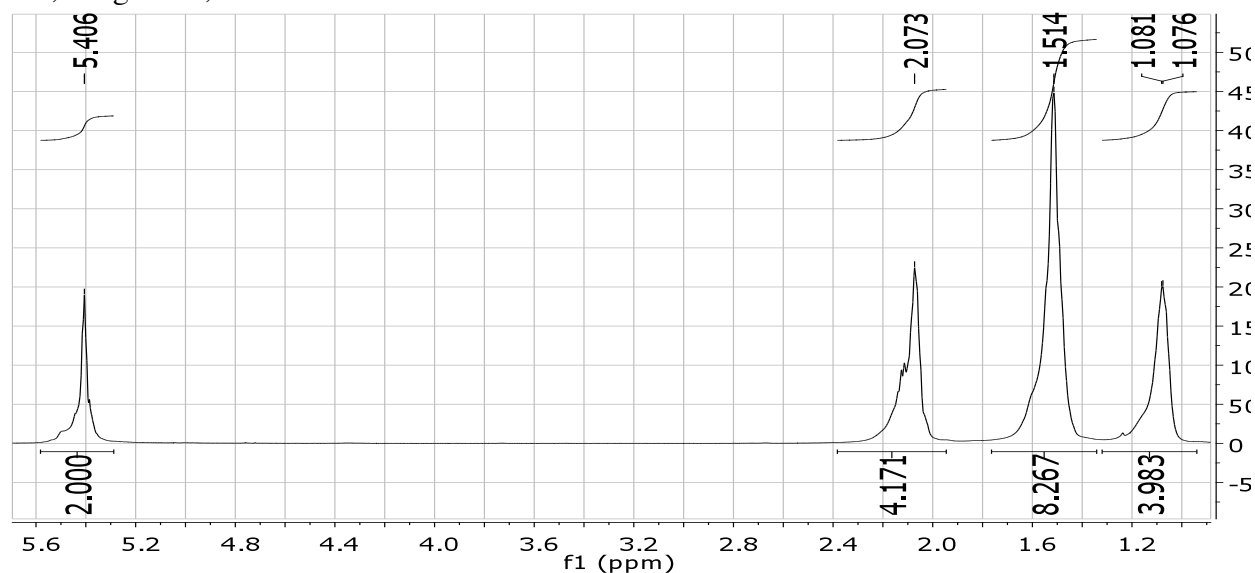


Figure S34: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 66.7 % *trans*-gDFC-PB.

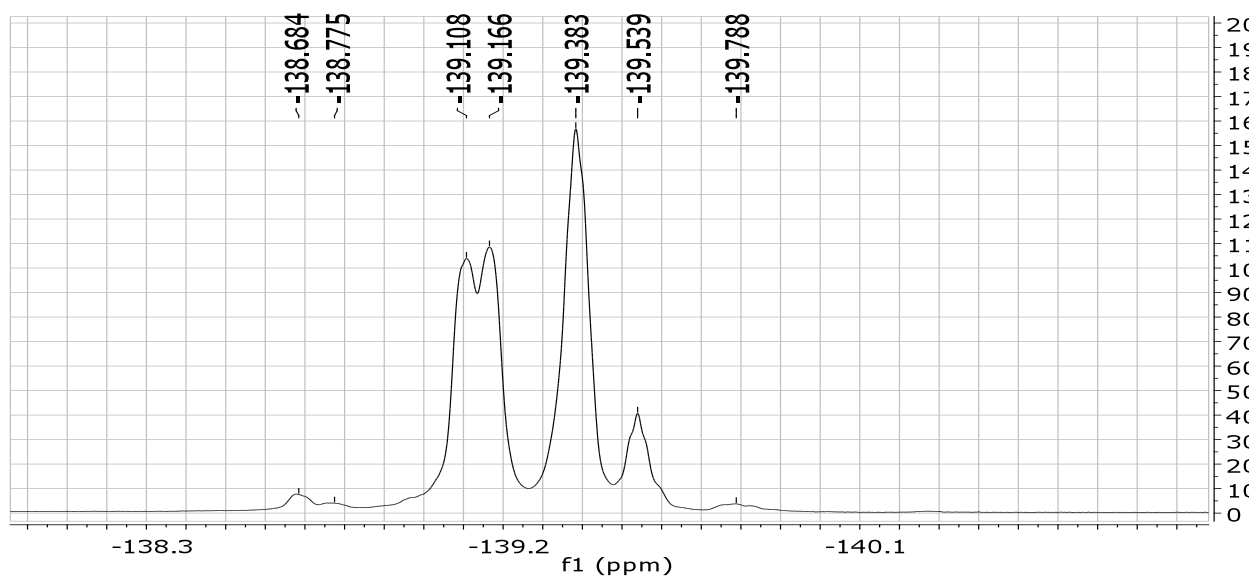


Figure S35: <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of 66.7 % *trans*-gDFC-PB.

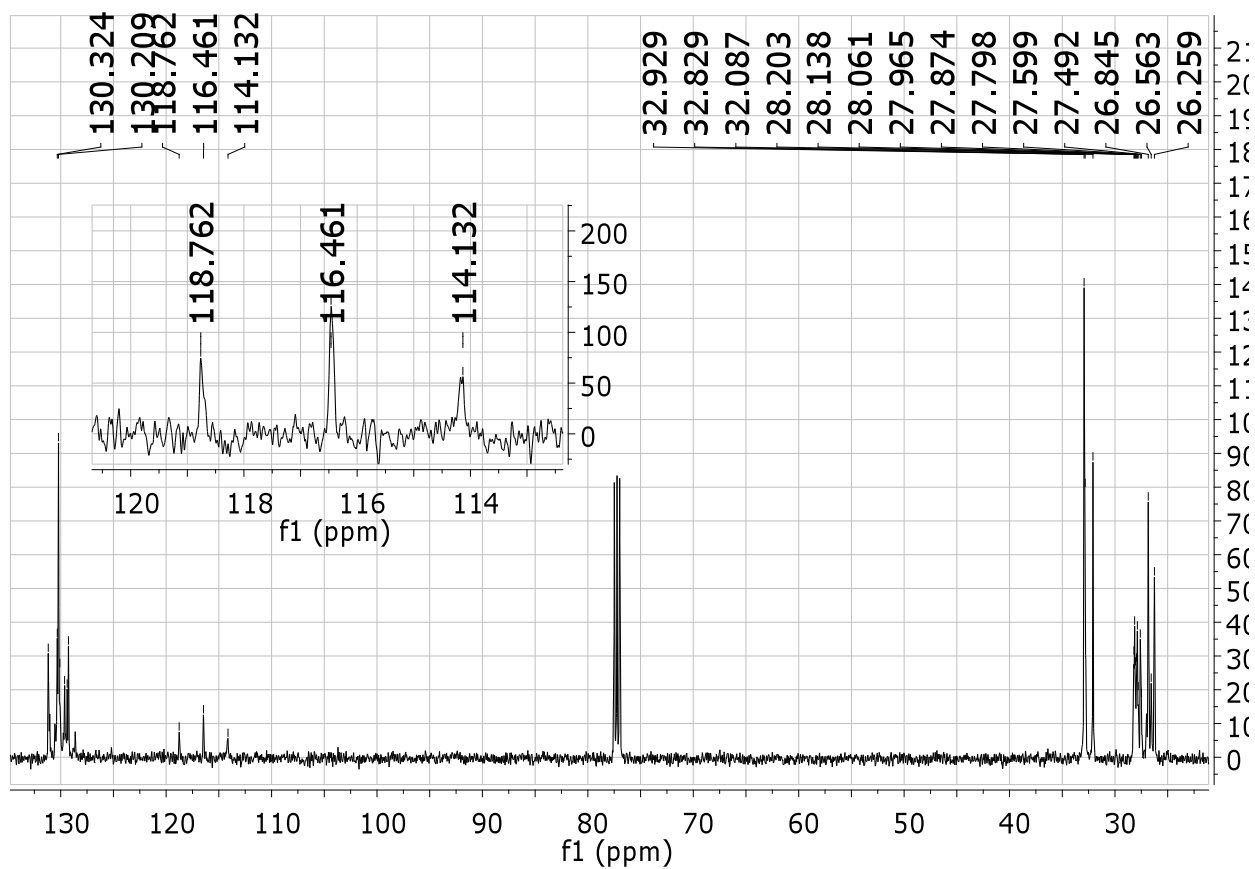


Figure S36: <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of 66.7 % *trans*-gDFC-PB. <sup>13</sup>CF<sub>2</sub> resonances at ~116 ppm.

### 261 kDa *c/t*-[36.1 % *g*DFC / 26.2 % *g*DCC]-PB

0.272 g 275 kDa 36.1 % *c/t*-*g*DFC-PB (2.41 mmoles double bonds) and 0.50 g (1.4 mmoles) CTAB were dissolved in 50 mL  $\text{CHCl}_3$  and deoxygenated with bubbling  $\text{N}_2$  for 30 minutes. In a separate round bottomed flask was dissolved 2.3 g (57.5 mmoles) NaOH and the solution was deoxygenated with bubbling  $\text{N}_2$  for 30 minutes. After 30 minutes the NaOH solution was added dropwise to the polymer/CTAB solution and the reaction was allowed to proceed for ~16 hours (overnight). The reaction was washed 3X with DI- $\text{H}_2\text{O}$ , brine and the polymer was precipitated with methanol. The polymer was reprecipitated twice more with methanol from  $\text{CH}_2\text{Cl}_2$  and dried on high vacuum.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.41 (b, 2.00H), 5.01 (b, 0.53H), 2.10 (b, 3.83H), 1.8-1.0 (b, 11.85H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.71, -125.06 (b, 1.0F), -139.13 (b, 2.43F), -154.20 (b, 0.93F).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.38, 141.62, 131.08, 130.30, 129.64, 129.54, 128.72, 116.41, 116.12, 115.32, 115.02, 67.17, 66.79, 66.39, 65.54, 65.20, 43.79, 35.91, 34.65, 32.81, 32.57, 32.35, 32.11, 31.77, 30.37, 30.00, 29.78, 29.54, 28.15, 27.47, 27.03, 26.86, 26.48, 26.26, 26.08, 25.13, 24.70, 21.85, 21.52, 21.21. Copolymer composition = 29.0 % 1,4-PB, 8.7 % 1,2-PB, 36.1 % *g*DFC [20.1 % *trans*-, 16.0 % *cis*-], 26.2 % *g*DCC. MALS-GPC ( $\text{dn dc}^{-1} = 0.0700 \text{ g mL}^{-1}$ ),  $M_N = 261,000$ ;  $M_W = 395,000 \text{ g mol}^{-1}$ , PDI = 1.51.

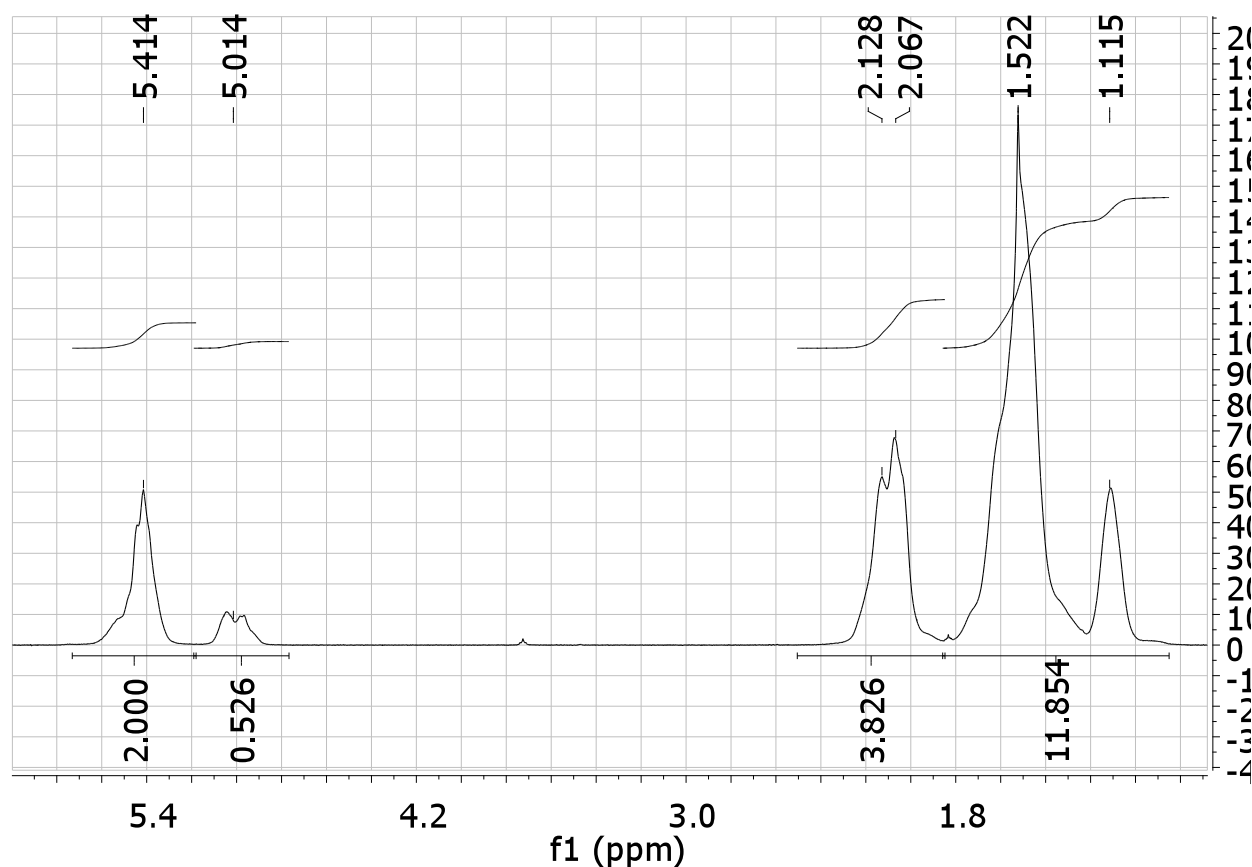


Figure S37:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 261 kDa *c/t*-[36.1 % *g*DFC / 26.2 % *g*DCC]-PB.

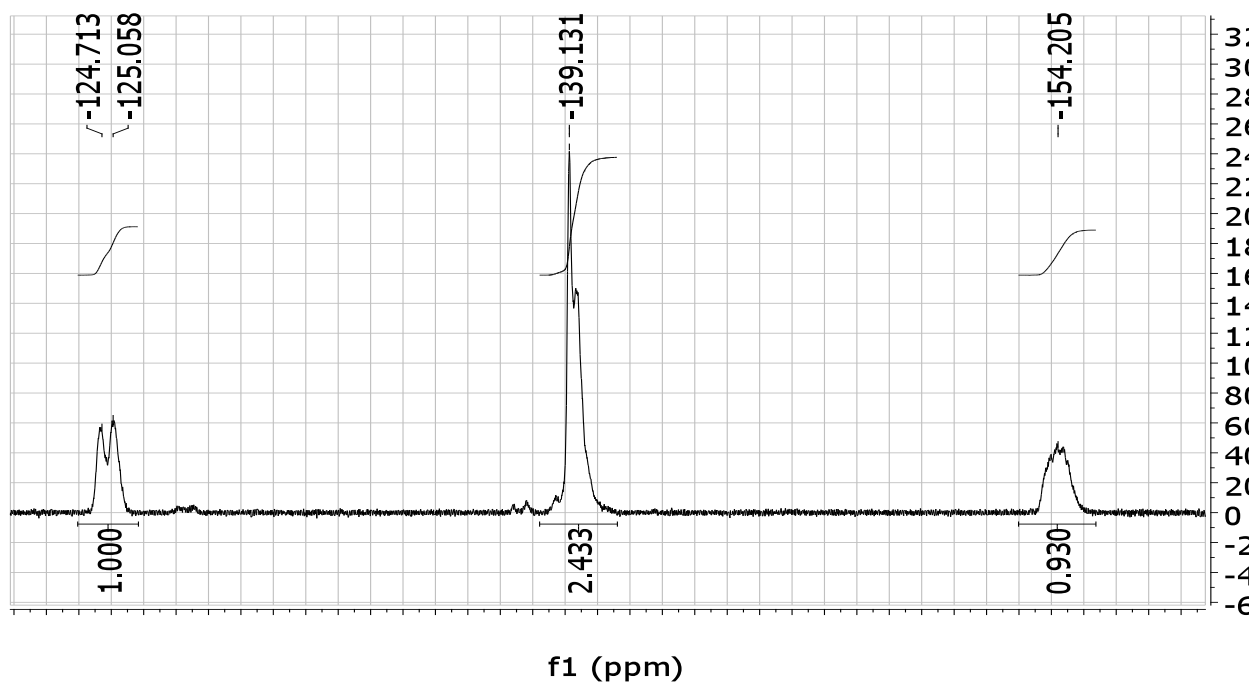


Figure S38: <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of 261 kDa *c/t*-[36.1 % gDFC / 26.2 % gDCC]-PB.

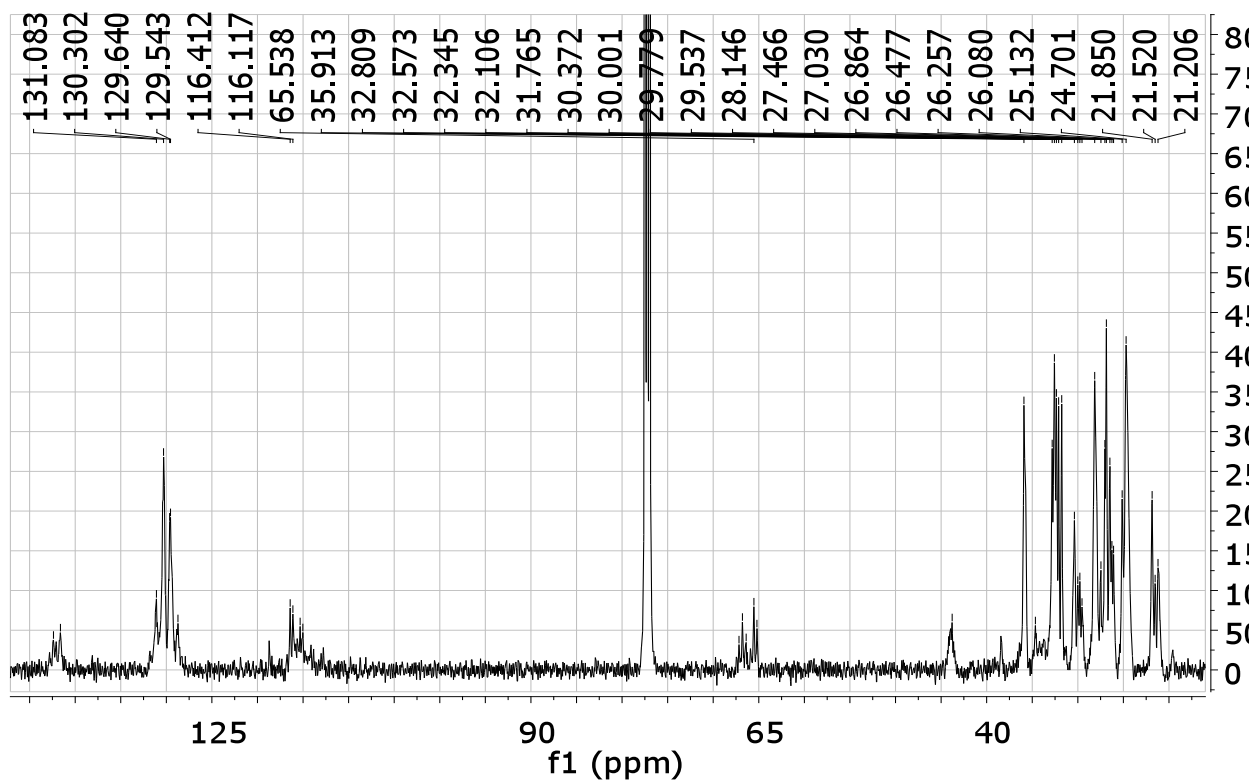


Figure S39: <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of 261 kDa *c/t*-[36.1 % gDFC / 26.2 % gDCC]-PB. <sup>13</sup>CF<sub>2</sub> resonances at ca. 116 ppm, <sup>13</sup>CCl<sub>2</sub> resonances at ca. 66 ppm.

## Ultrasound Experiments

### 96.8 kDa 3.8 % *c/t*-gDFC-PB

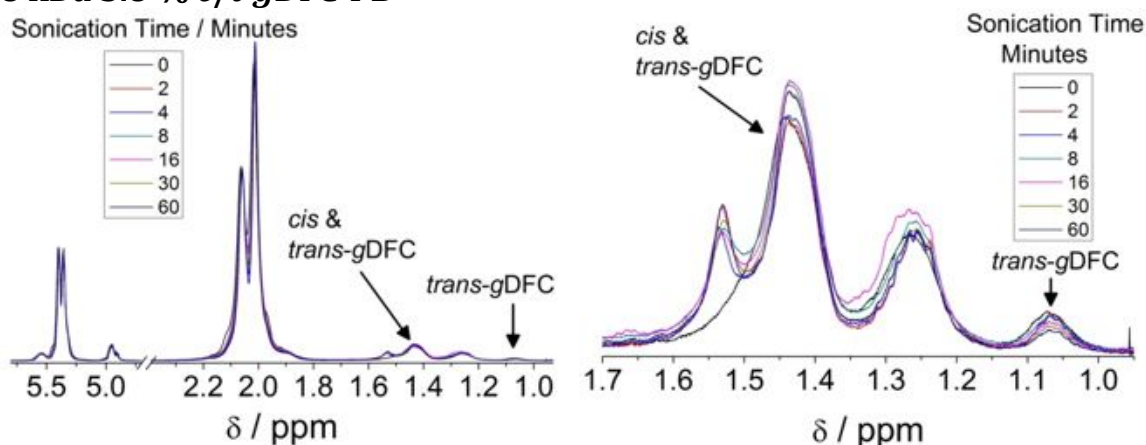


Figure S40: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) and closeup (right) of *gDFC* resonances of 3.8 % *c/t*-gDFC-PB during sonication. Resonance at  $\sim 1.54$  ppm is residual  $\text{H}_2\text{O}$ .

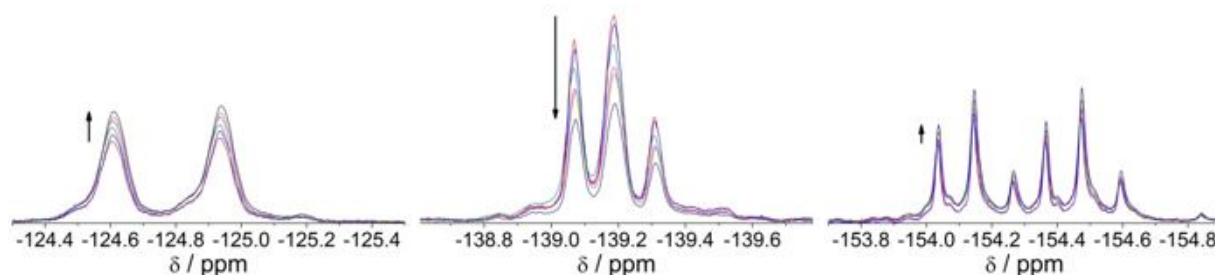


Figure S41: Select regions of the  $^{19}\text{F}$ -NMR spectrum (470 MHz,  $\text{CDCl}_3$ ) of *gDFC* resonances ( $-124.8$ ,  $-154.3$  ppm = *cis*;  $-139.2$  = *trans*) during sonication of 3.8 % *c/t*-gDFC-PB.

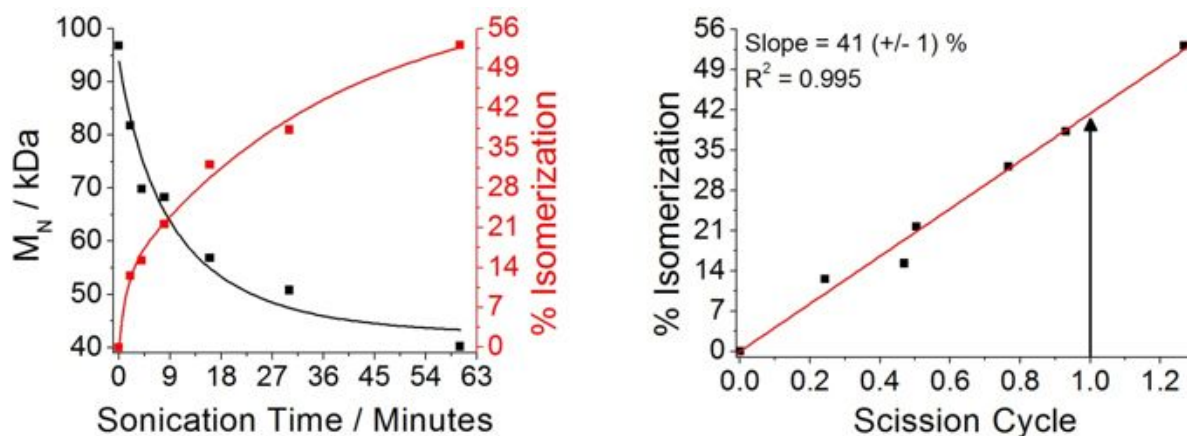


Figure S42: Sonication of 3.8 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $41 \pm 1$  % isomerization per scission cycle.



## 192 kDa 8.0 % *c/t*-gDFC-PB

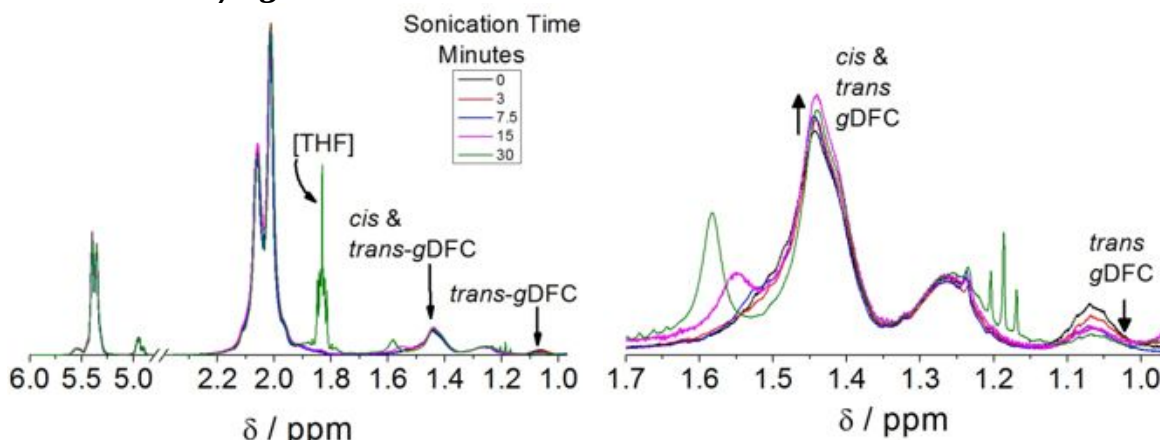


Figure S43: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 8.0 % *c/t*-gDFC-PB during sonication.

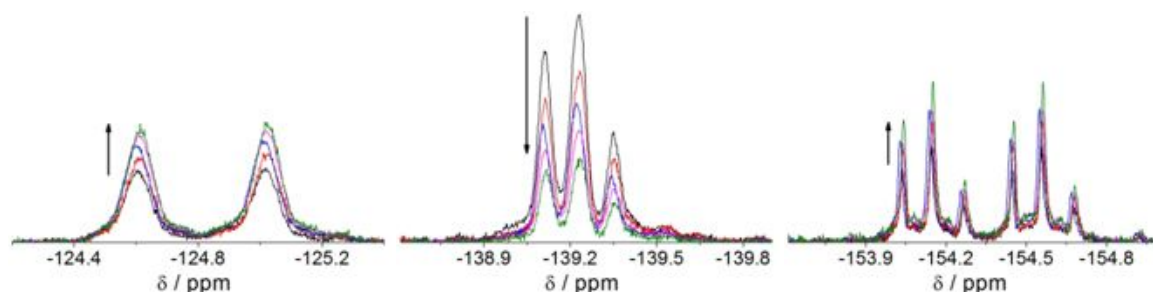


Figure S44: Select regions of the  $^{19}\text{F}$ -NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 8.0 % *c/t*-gDFC-PB.

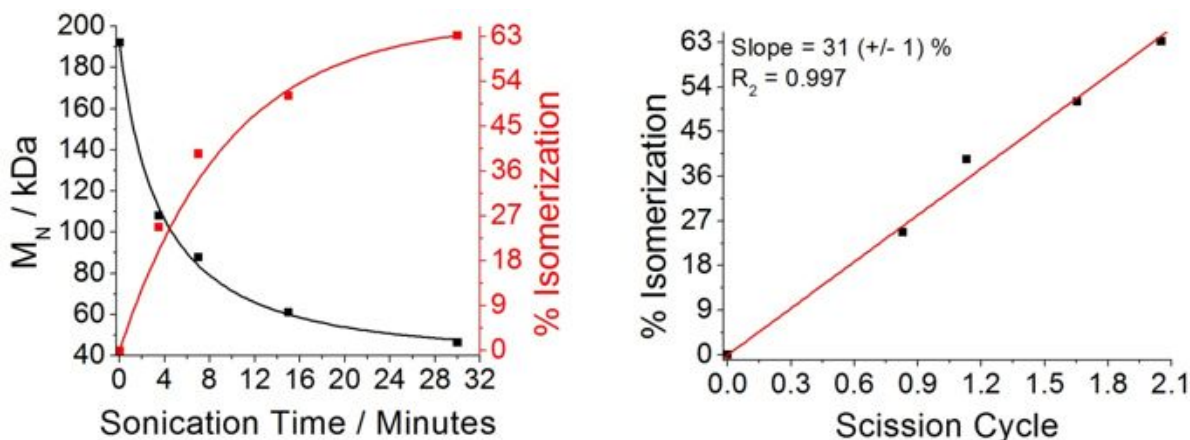


Figure S45: Sonication of 8.0 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $31 \pm 1$  % isomerization per scission cycle.

## 179 kDa 9.1 % *c/t*-gDFC-PB

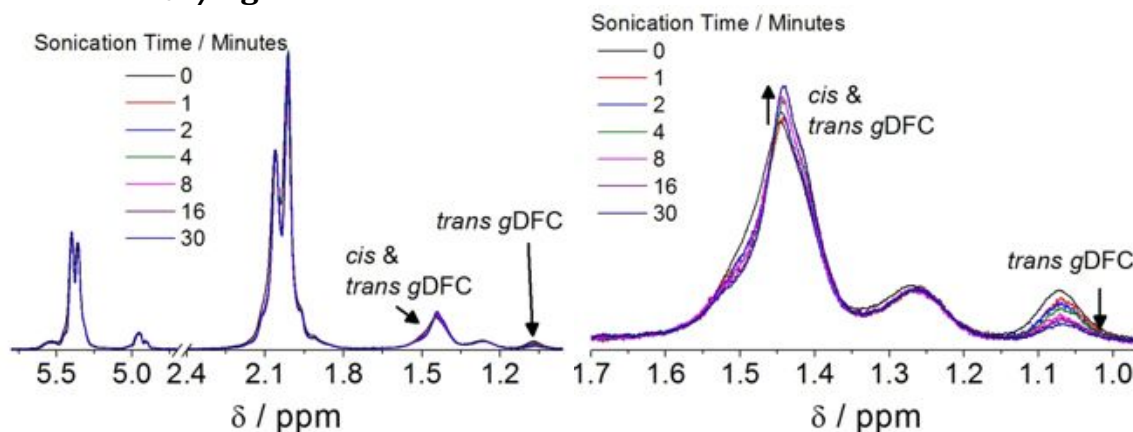


Figure S46:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) during sonication of 9.1 % *c/t*-gDFC-PB.

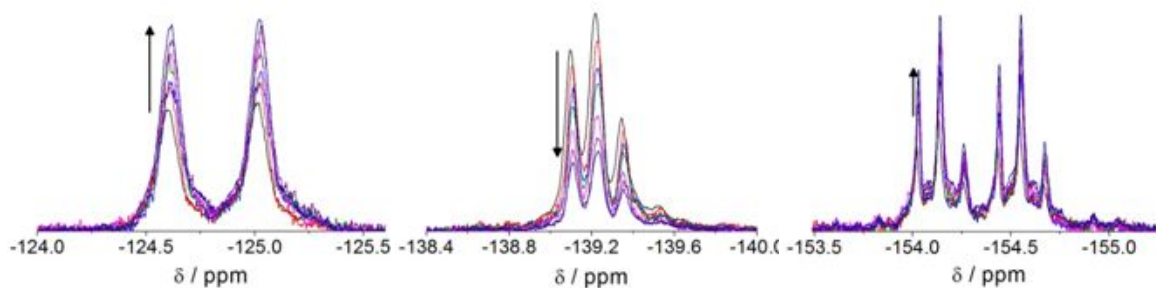


Figure S47:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) during sonication of 9.1 % *c/t*-gDFC-PB.

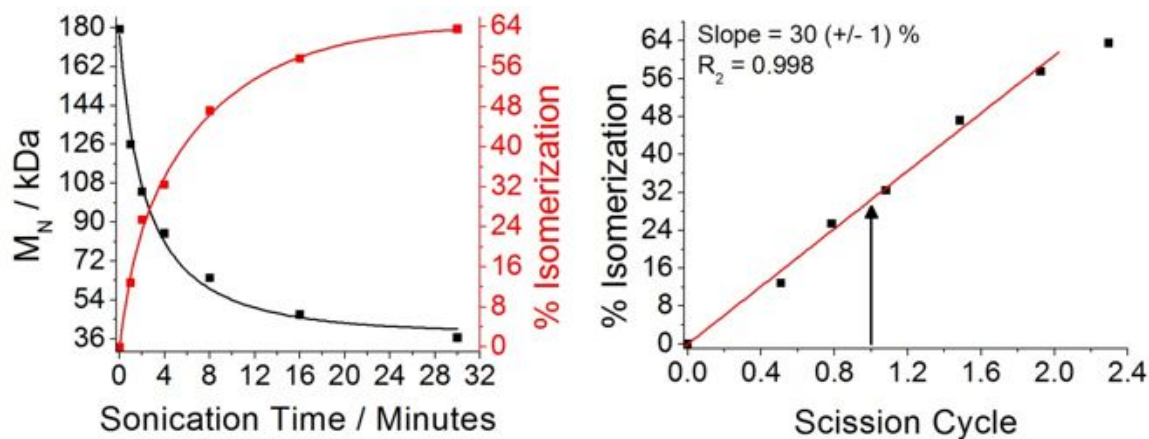


Figure S48: Molecular weight degradation and percent isomerization versus sonication time and a plot of the isomerization versus the polymer scission cycle leads to 30 % isomerization  $\text{SC}^{-1}$ .

### 154 kDa 10.9 % *c/t*-gDFC-PB

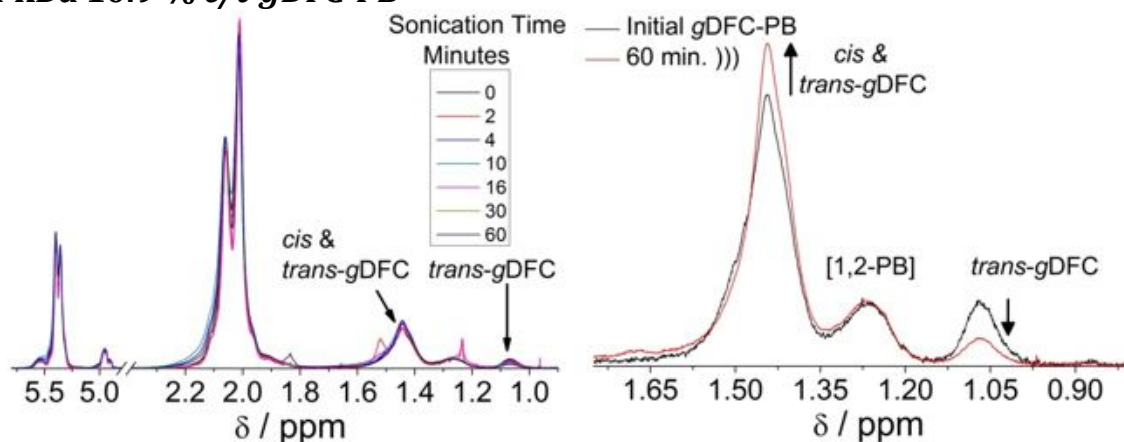


Figure S49: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 10.9 % *c/t*-gDFC-PB during sonication.

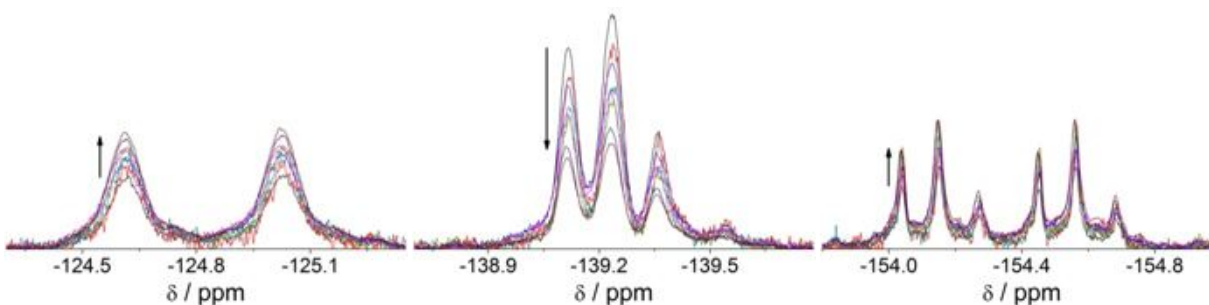


Figure S50: Select regions of the  $^{19}\text{F}$ -NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 10.9 % *c/t*-gDFC-PB.

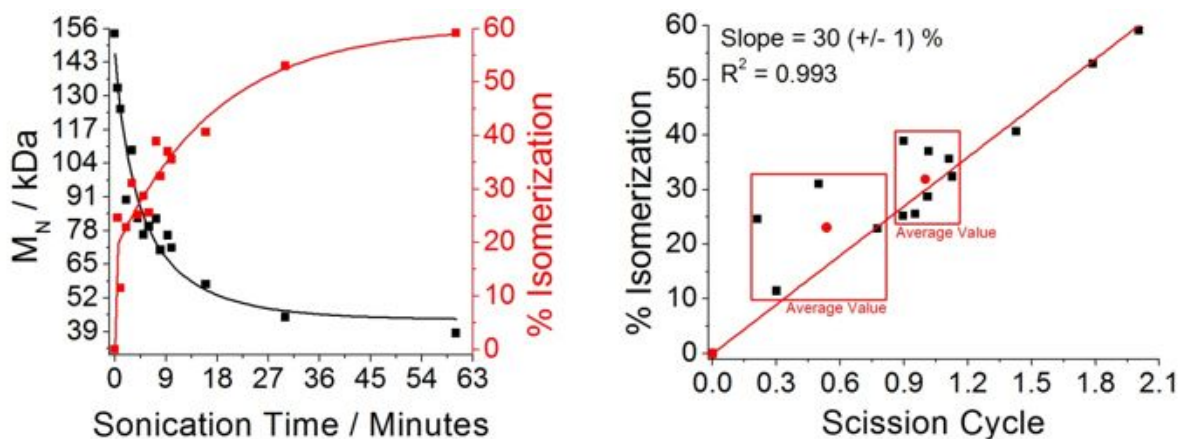


Figure S51: Sonication of 10.9 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $30 \pm 1$  % isomerization per scission cycle. Due to the large variability in the data, average values (noted in red circles) were used in the linear regression.

## 190 kDa 22.0 % *c/t*-gDFC-PB

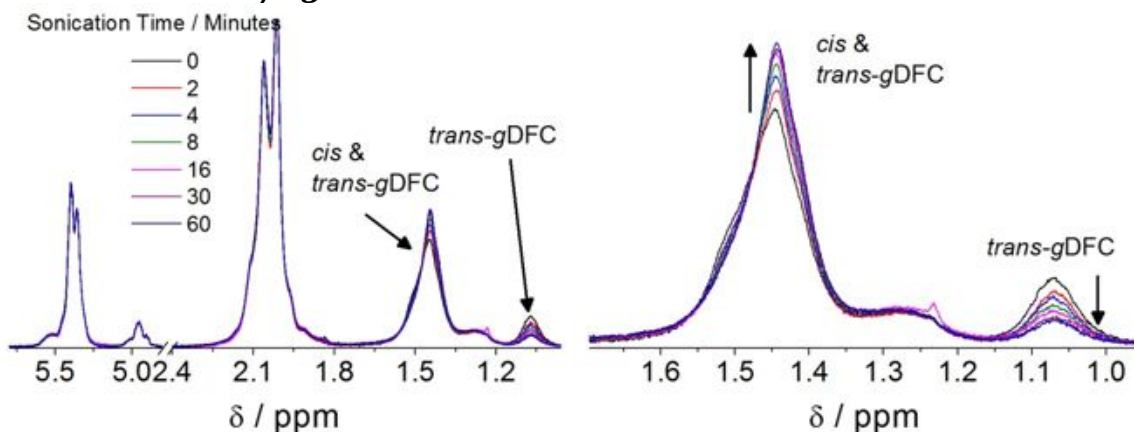


Figure S52:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) during sonication of 22 % *c/t*-gDFC-PB.

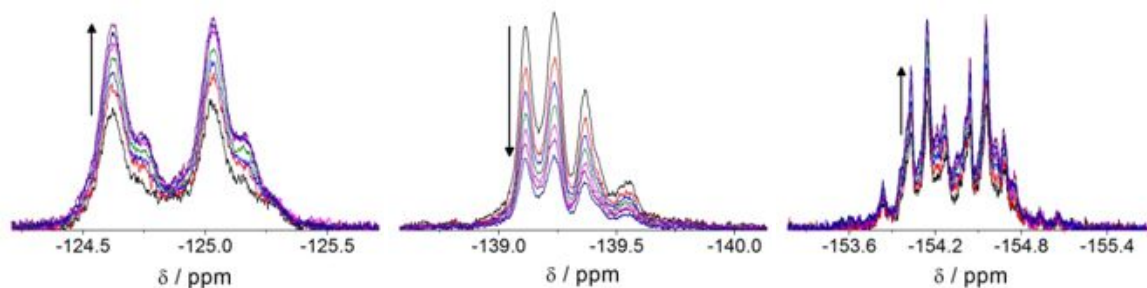


Figure S53:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) during sonication of 22 % *c/t*-gDFC-PB.

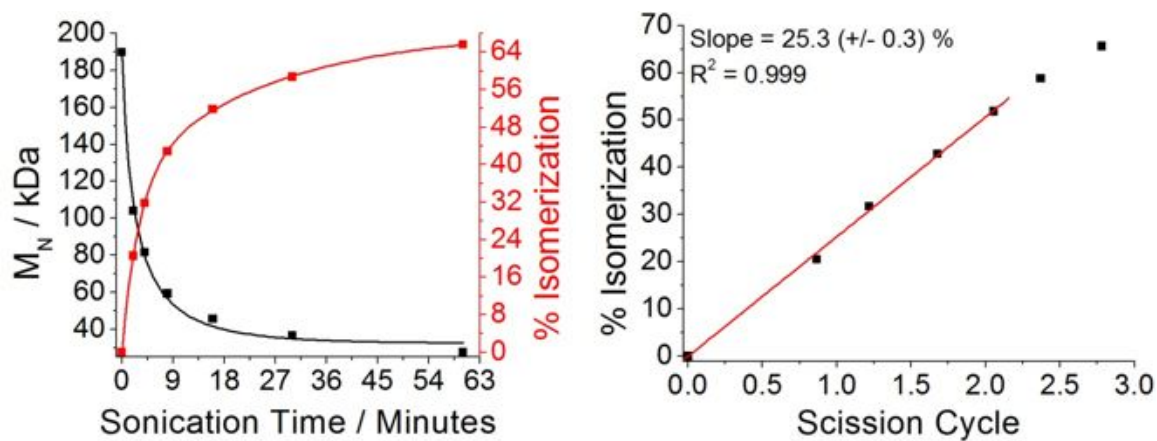


Figure S54: Molecular weight degradation and isomerization profiles and a plot of the isomerization versus the polymer scission cycle leads to 25 % isomerization after the first scission cycle.



### 319 kDa 32.4 % *c/t*-gDFC-PB

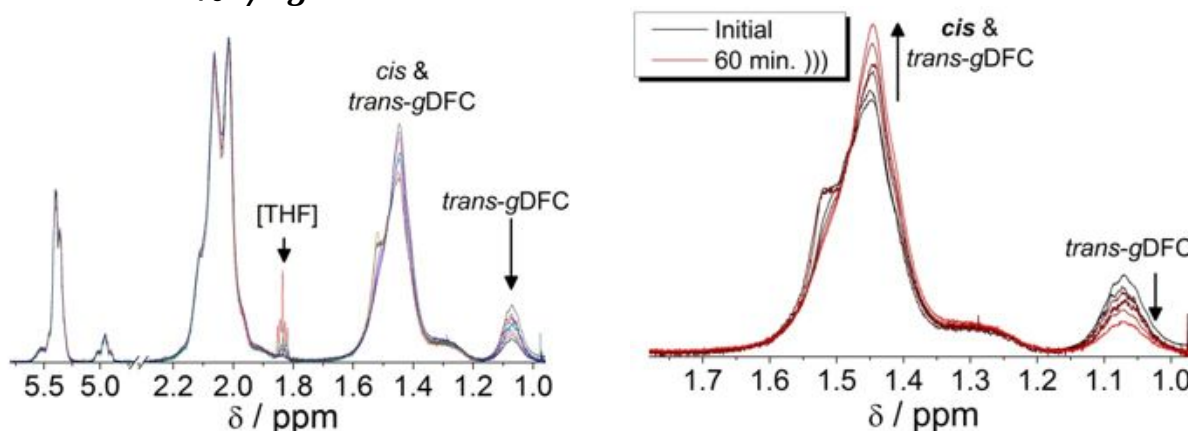


Figure S55: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 32.4 % *c/t*-gDFC-PB during sonication.

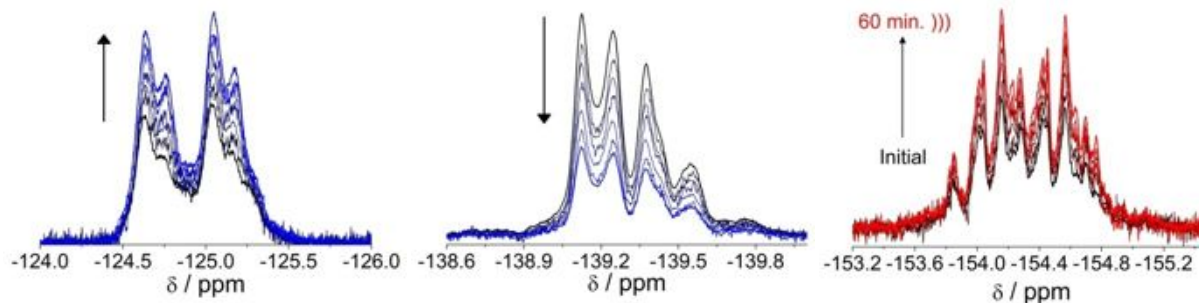


Figure S56: Select regions of the  $^{19}\text{F}$ -NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 32.4 % *c/t*-gDFC-PB.

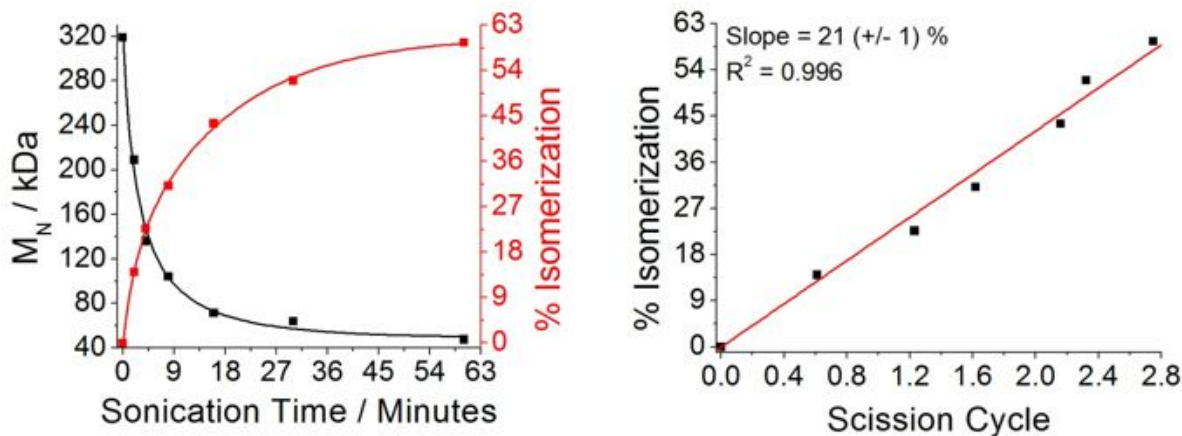


Figure S57: Sonication of 32.4 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $21 \pm 1$  % isomerization per scission cycle.

## 275 kDa 36.1 % *c/t*-gDFC-PB

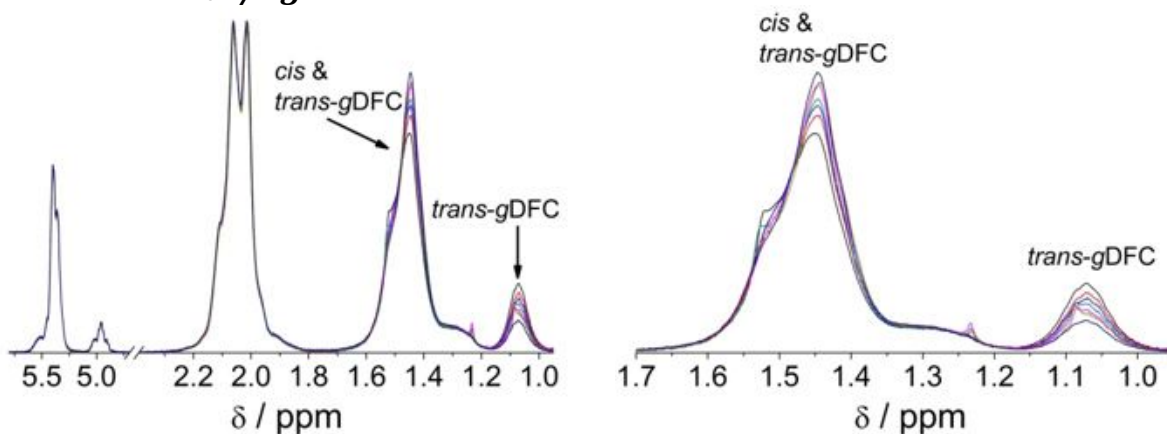


Figure S58: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 36.1 % *c/t*-gDFC-PB during sonication.

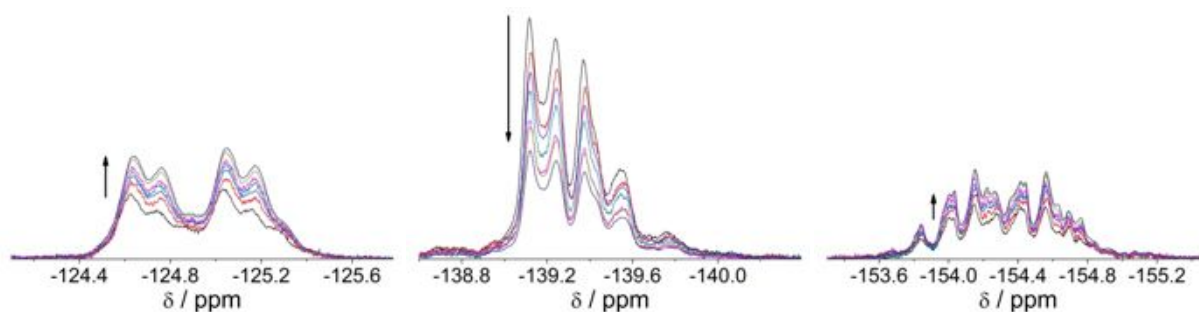


Figure S59: Select regions of the  $^{19}\text{F}$ -NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 36.1 % *c/t*-gDFC-PB.

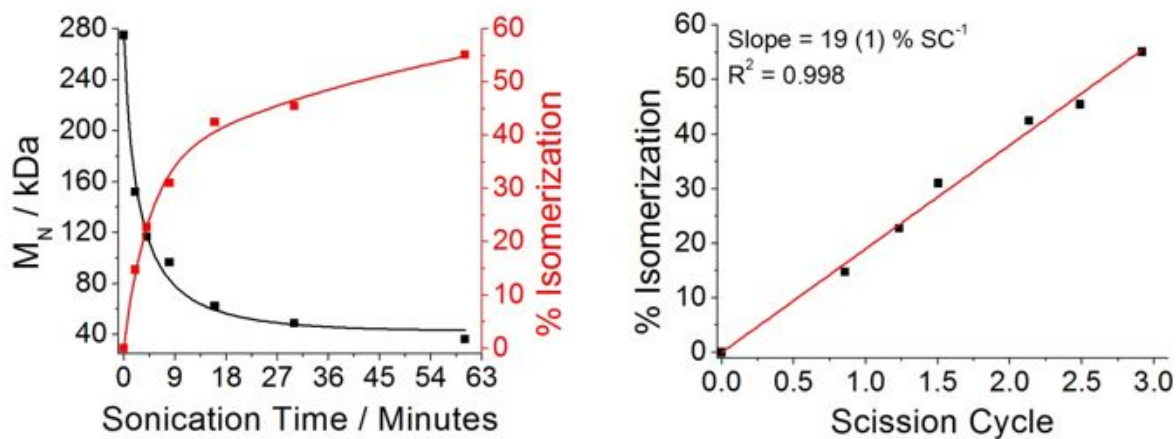


Figure S60: Sonication of 36.1 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $19 \pm 1$  % isomerization per scission cycle.

# 173 kDa 47.4 % *c/t*-gDFC-PB

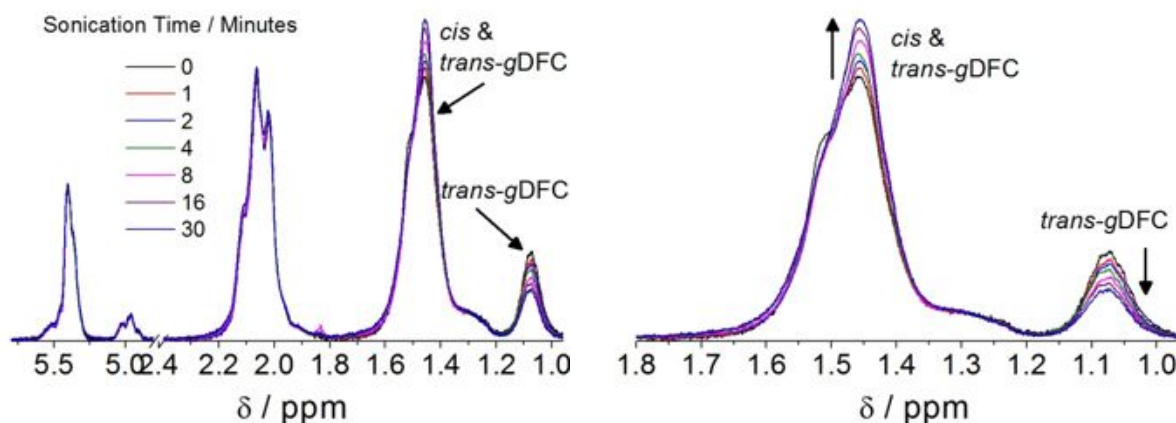


Figure S61:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) during sonication of 47.4 % *c/t*-gDFC-PB.

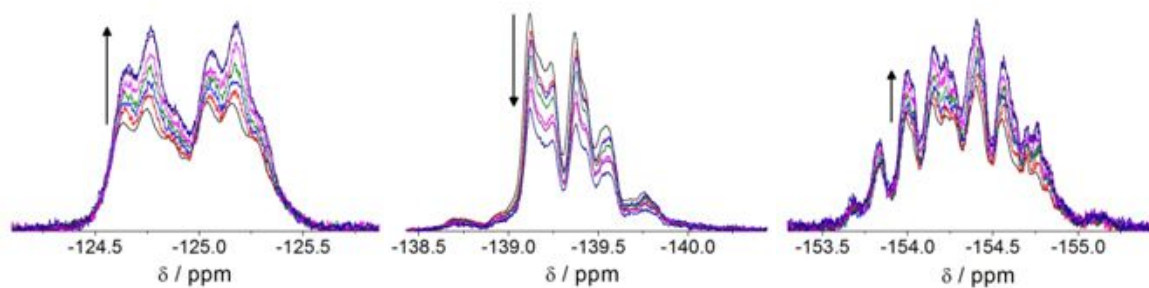


Figure S62:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) during sonication of 47.4 % *c/t*-gDFC-PB.

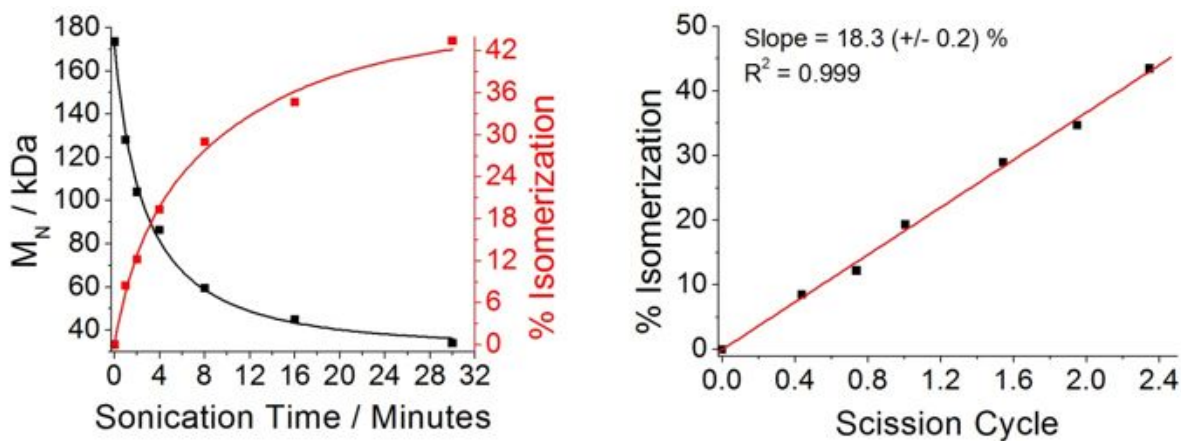


Figure S63: Molecular weight degradation and isomerization versus sonication time and a plot of the isomerization versus the polymer scission cycle is linear with a slope of 18.3 %.

## 290 kDa 51.7 % *c/t*-gDFC-PB

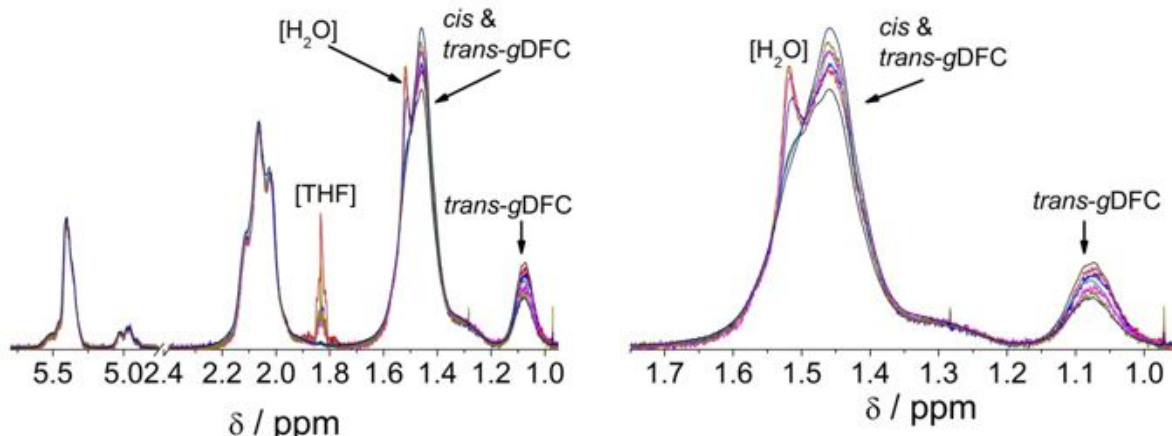


Figure S64: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 51.7 % *c/t*-gDFC-PB during sonication.

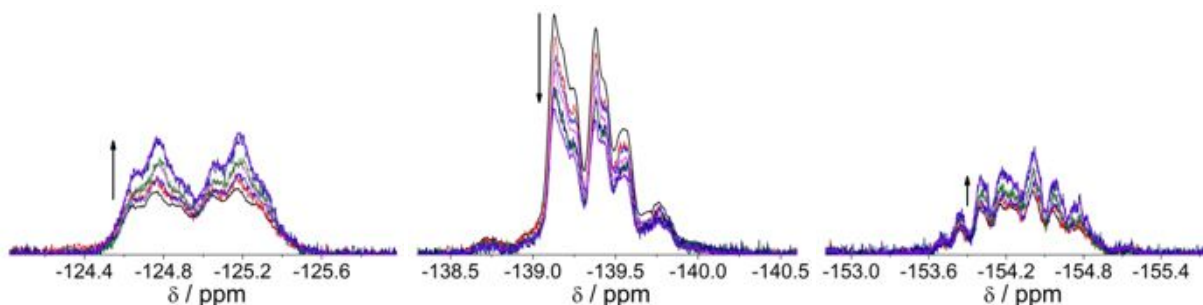


Figure S65: Select regions of the  $^{19}\text{F}$ -NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 51.7 % *c/t*-gDFC-PB.

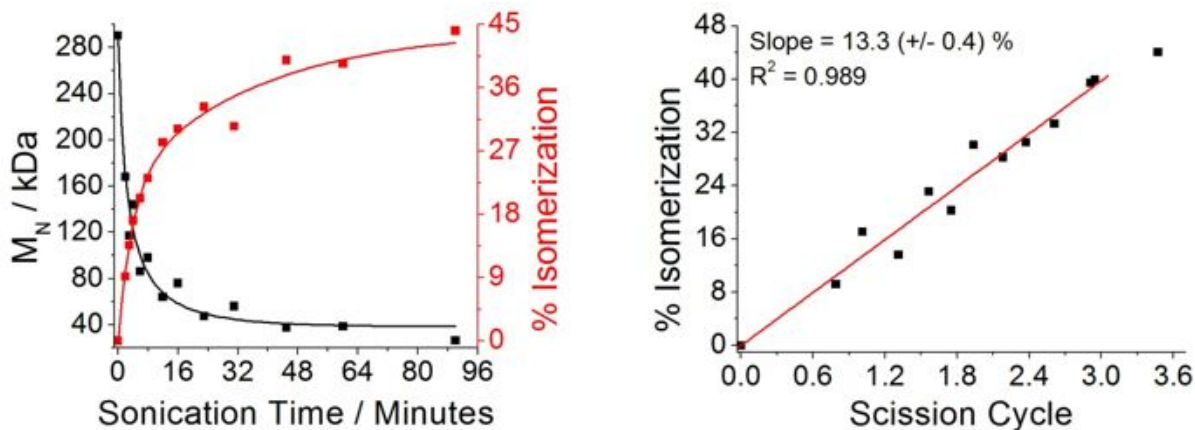


Figure S66: Sonication of 51.7 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $13.3 \pm 0.4$  % isomerization per scission cycle.



### 88.4 kDa 58.7 % *c/t*-gDFC-PB

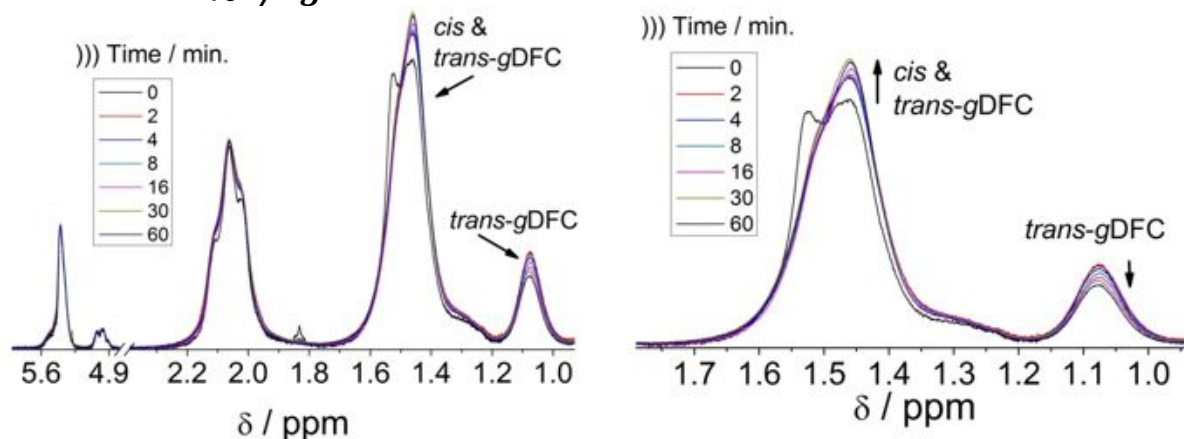


Figure S67: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 58.7 % *c/t*-gDFC-PB during sonication.

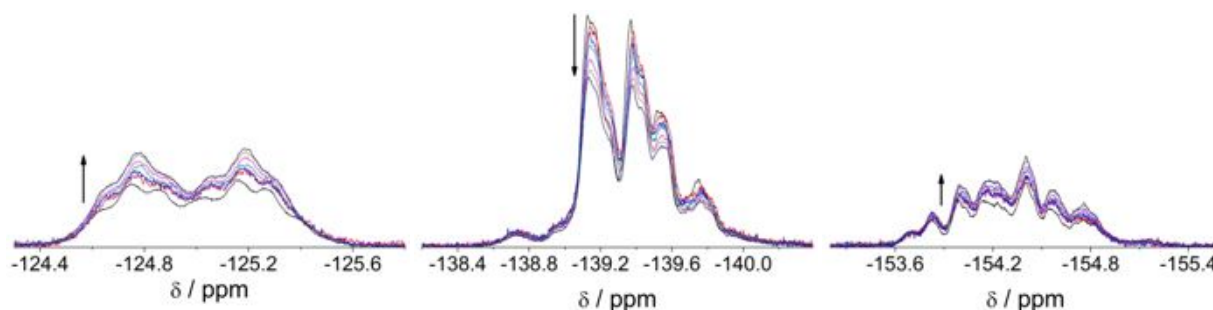


Figure S68: Select regions of the  $^{19}\text{F}$ -NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 58.7 % *c/t*-gDFC-PB.

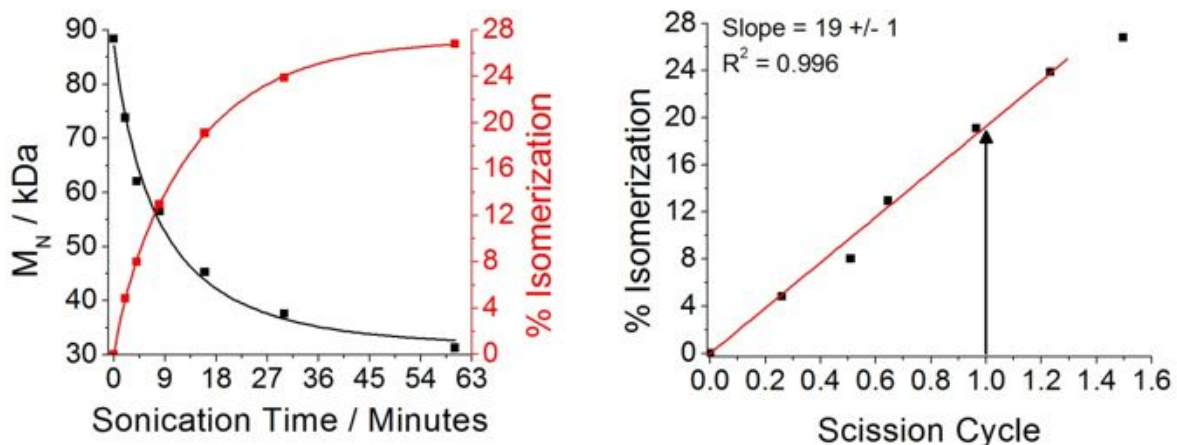


Figure S69: Sonication of 58.7 % *c/t*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $18.7 \pm 0.4$  % isomerization per scission cycle.

## 177 kDa 95.1 % *c/t*-gDFC-PB

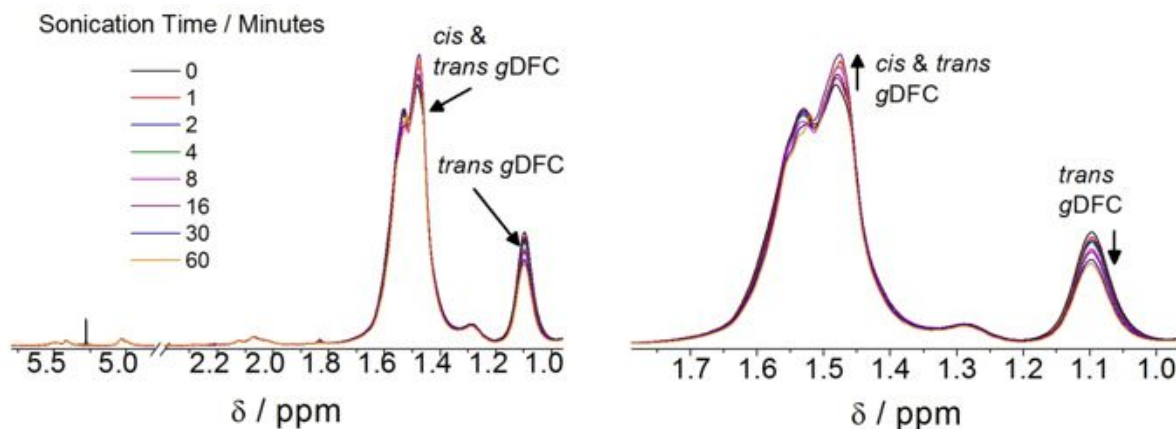


Figure S70:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectra during sonication of 95.1 % *c/t*-gDFC-PB (full spectra, left and zoomed region, right).

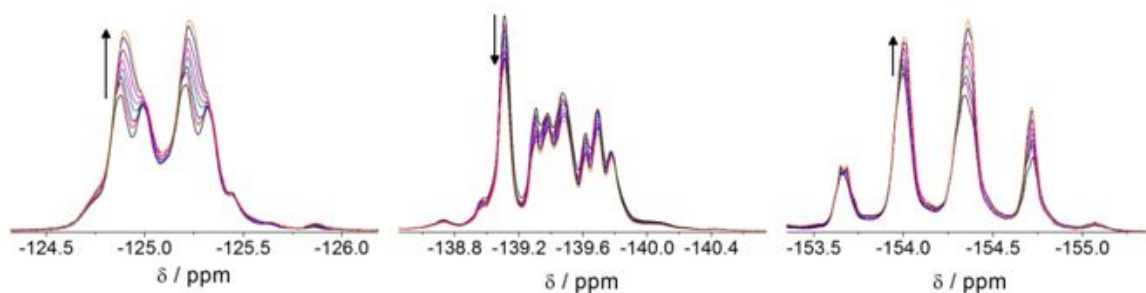


Figure S71:  $^{19}\text{F}$  NMR spectra (470 MHz,  $\text{CDCl}_3$ ) taken during sonication of 95.1 % *c/t*-gDFC-PB.

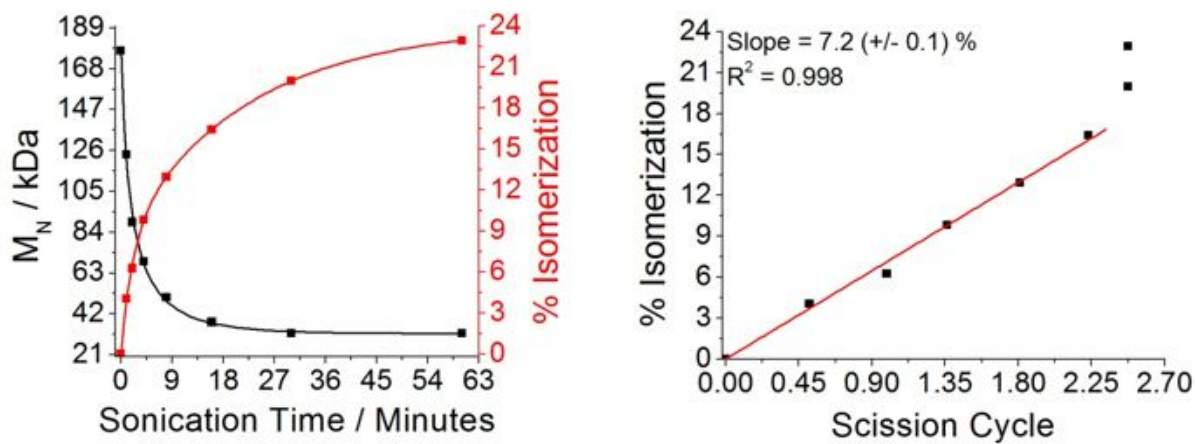


Figure S72: Molecular weight degradation and isomerization profiles (left) and a fit of the % isomerization after the first scission cycle is linear with a slope of  $7.2 \pm 0.1$  % isomerization.

65.5 kDa kDa 33.3 % *trans*-gDFC-PB [ROMP]

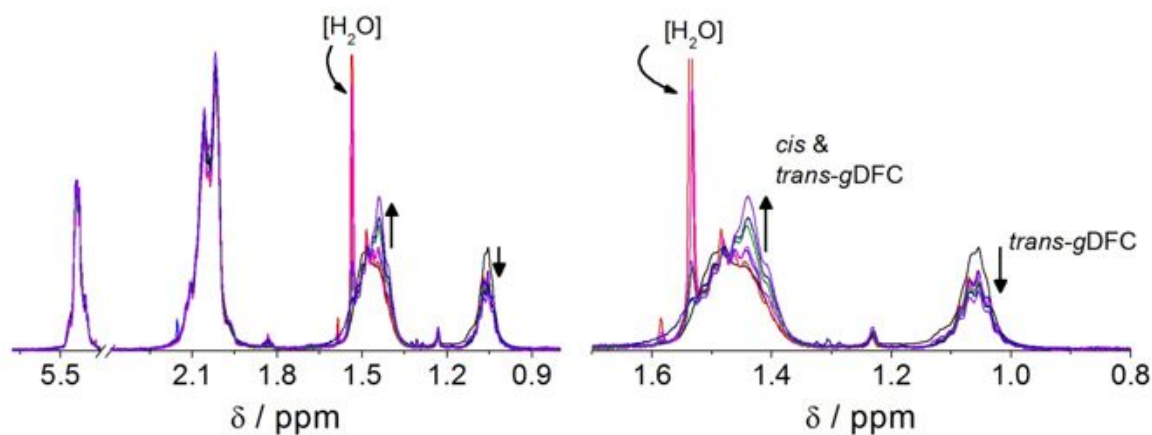


Figure S73: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 33 % *trans*-gDFC-PB during sonication.

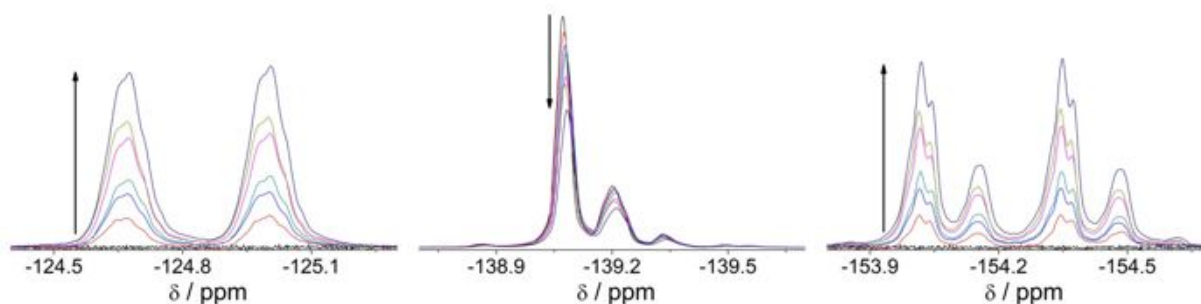


Figure S74: Select regions of the  $^{19}\text{F}$ -NMR spectrum (470 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 33 % *trans*-gDFC-PB.

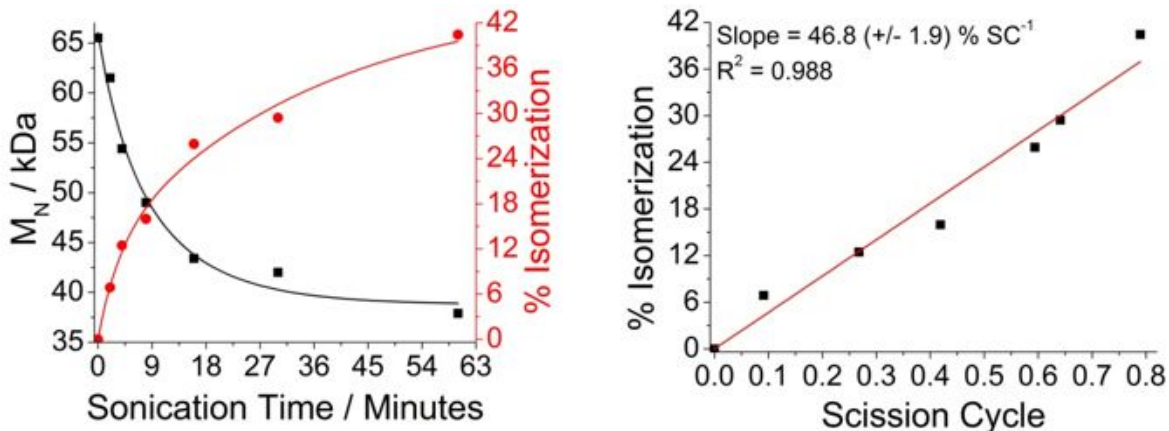


Figure S75: Sonication of 33 % *trans*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $47 \pm 2$  % isomerization per scission cycle.

66.2 kDa 66.7 % *trans*-gDFC-PB [ROMP]

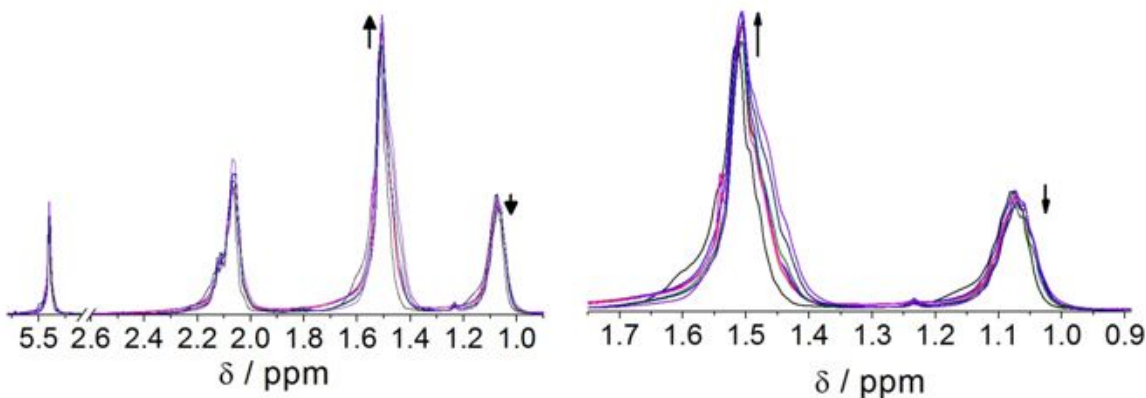


Figure S76: Full  $^1\text{H}$ -NMR (left, 400 MHz,  $\text{CDCl}_3$ ) spectra and closeup (right) of gDFC resonances of 66 % *trans*-gDFC-PB during sonication.

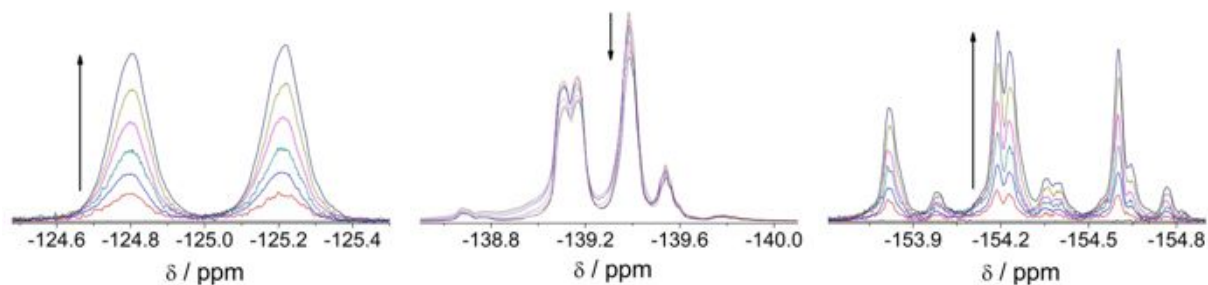


Figure S77: Select regions of the  $^{19}\text{F}$ -NMR spectrum (470 MHz,  $\text{CDCl}_3$ ) of gDFC resonances (-124.8, -154.3 ppm = *cis*; -139.2 = *trans*) during sonication of 66 % *trans*-gDFC-PB.

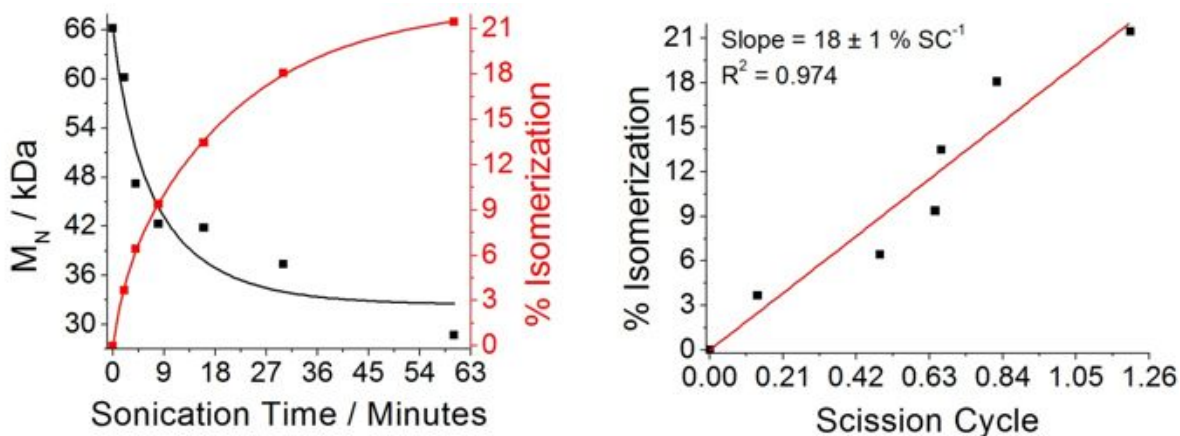


Figure S78: Sonication of 66 % *trans*-gDFC-PB shows the isomerization is dependent on the degradation of the copolymer molecular weight (left). A plot of the amount of isomerization per polymer scission cycle is linear with a slope of  $18 \pm 1$  % isomerization per scission cycle.

261 kDa *c/t*-[36.1 % *g*DFC / 26.2 % *g*DCC]-PB

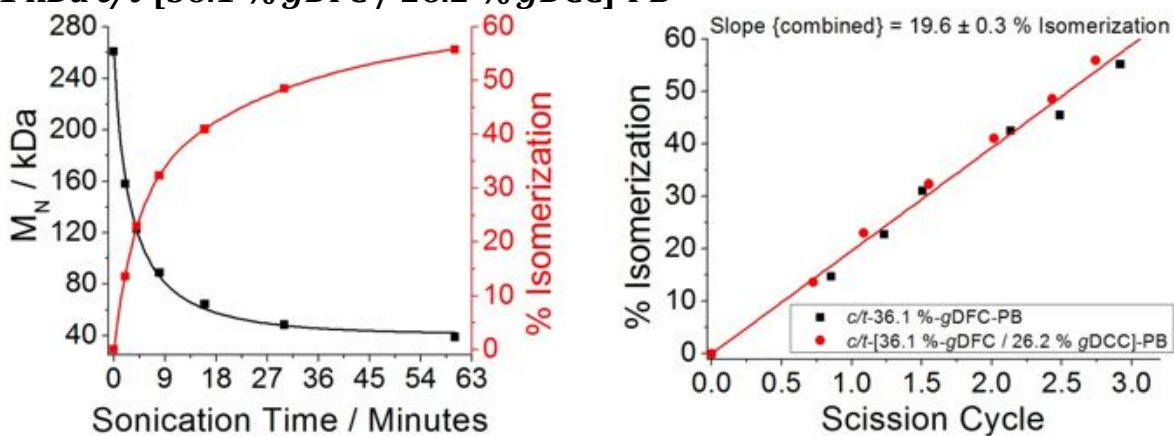


Figure S79: Molecular weight degradation and % isomerization profiles (right) during sonication of mixed *c/t*-*g*DFC-*g*DCC-PB copolymer. The isomerization after 1 scission cycle is equivalent to the initially sonicated 36.1 % *c/t*-*g*DFC-PB copolymer.

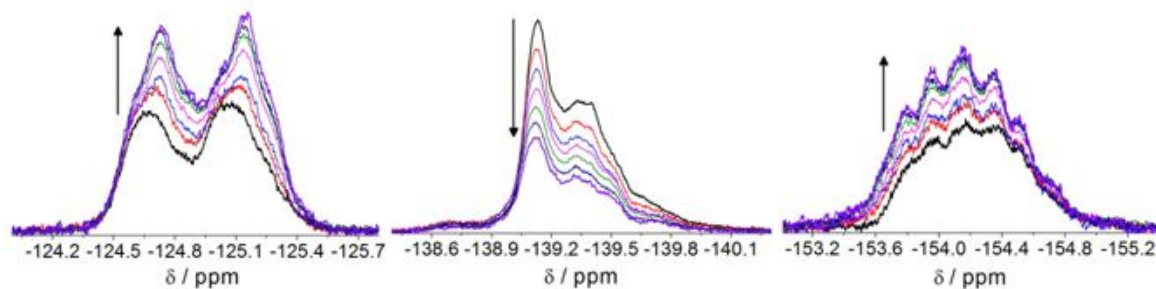


Figure S80:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) during sonication of mixed *c/t*-*g*DFC-*g*DCC-PB copolymer shows the loss of *trans* isomer and formation of the *cis*-*g*DFCs.

## Product Analysis: Coupled Diradical Disproportionation

**\*\*No new alkene resonances are observed after sonication of *cis/trans*-PB.\*\***

### *cis/trans*-PB

100 mg *c/t*-PB was dissolved in 60 mL THF and deoxygenated for 30 minutes. The solution was subjected to pulsed ultrasound (30 % amplitude, THF, 6-9 °C, N<sub>2</sub>) for 30 minutes in 15 mL portions. After pulsed ultrasound the solutions were recombined and subjected to GPC and NMR.  $M_N(i) = 194,000 \text{ g mol}^{-1}$ ;  $M_N(30 \text{ minutes}) = 59,900 \text{ g mol}^{-1}$ .

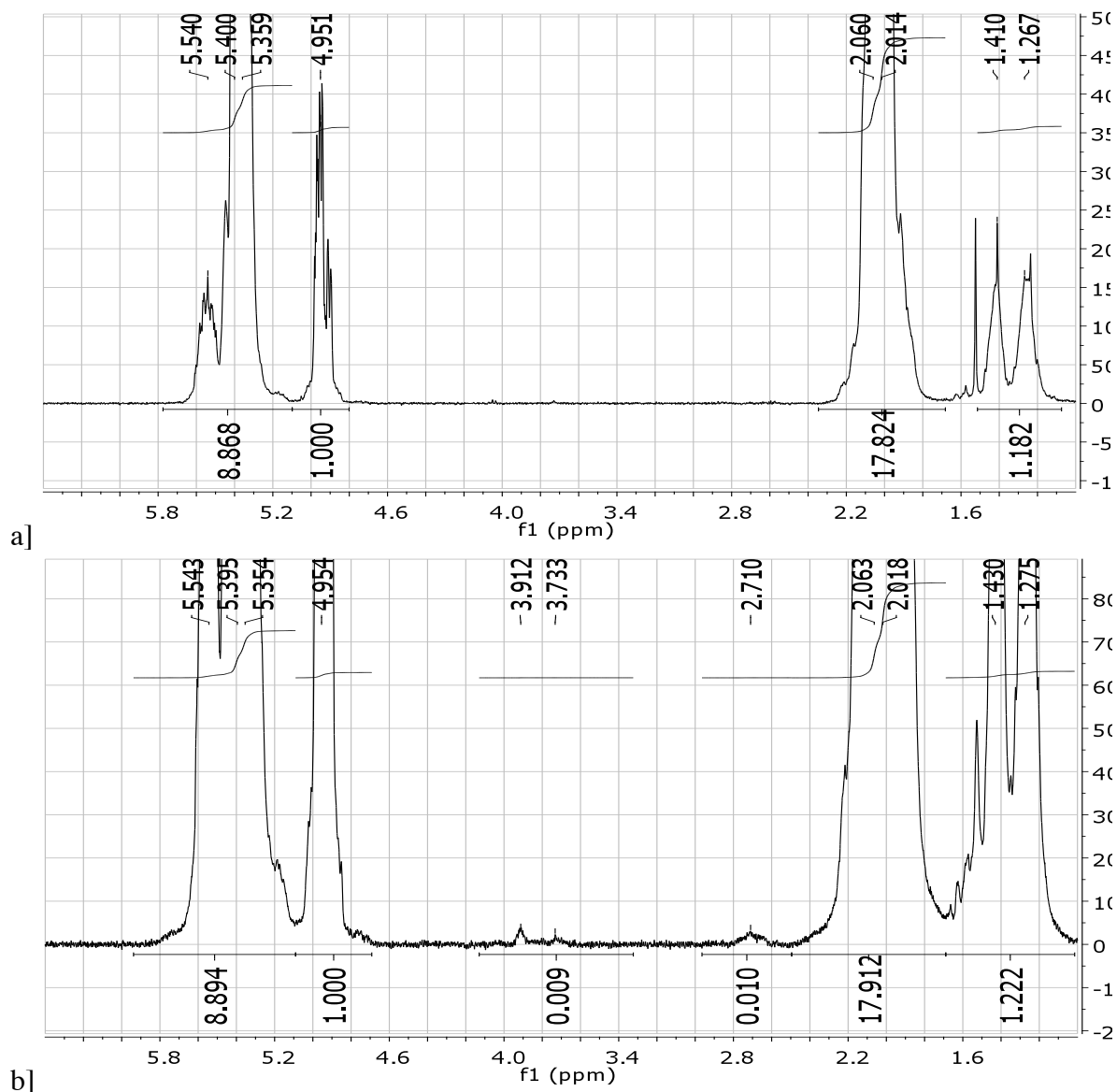


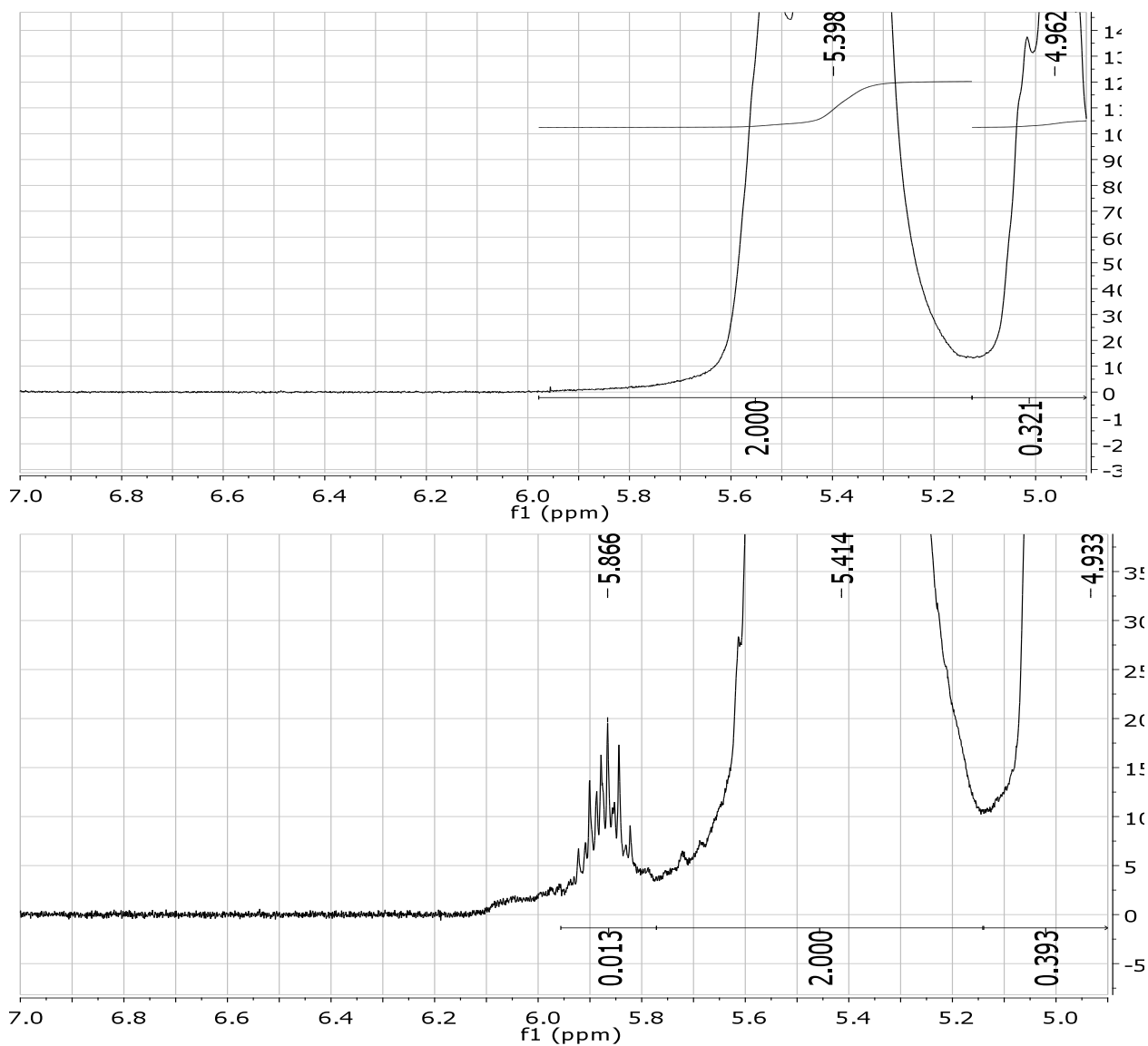
Figure S81. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) observed before [a] and after [b] sonication of *c/t*-PB.



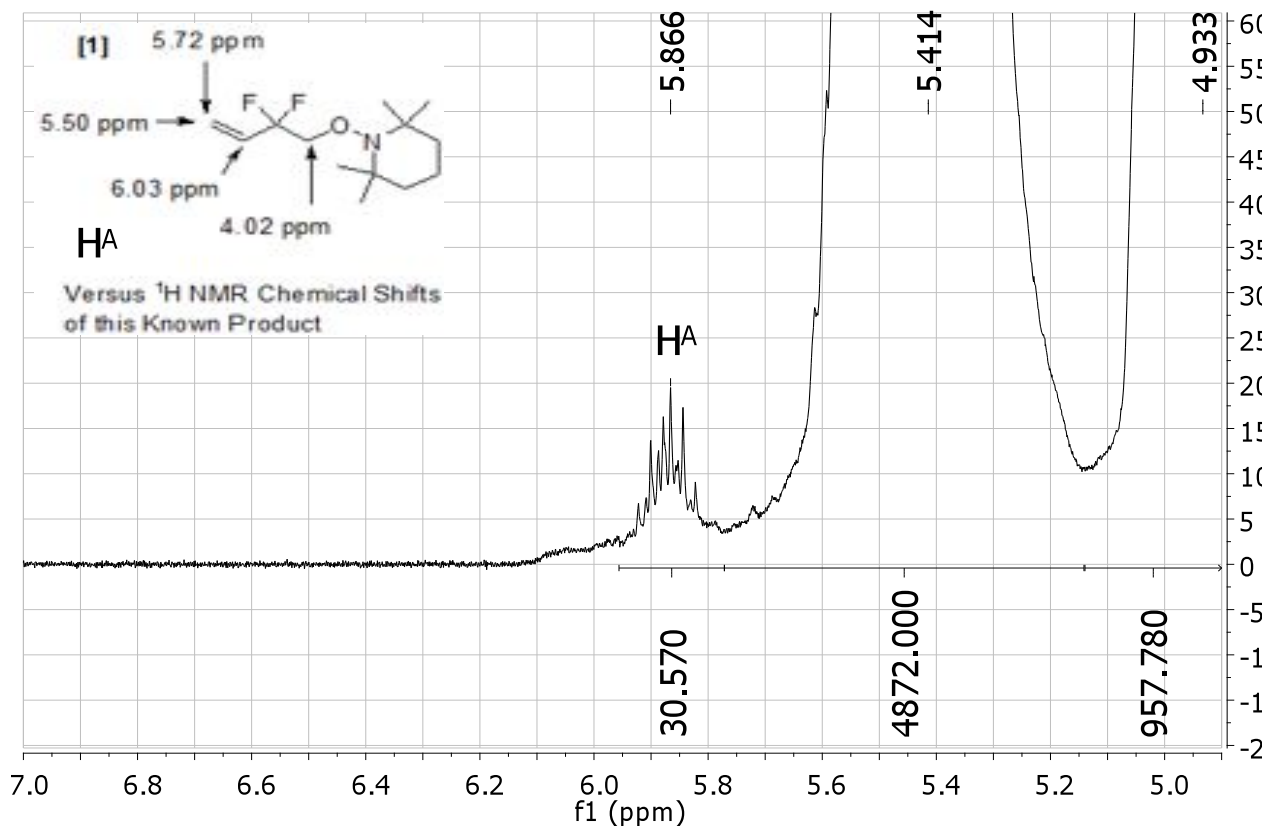
## 275 kDa 36 % *c/t-g*DFC-PB ))) , 3 hours

**\*\*New alkene resonance is observed after sonication of 36 % *c/t-g*DFC-PB.\*\***

42 mg polymer was dissolved in 15 mL THF and deoxygenated with bubbling N<sub>2</sub> for 30 minutes. After 30 minutes the solution was subjected to pulsed ultrasound (35 % amplitude, N<sub>2</sub>, 6-9 °C) for 3 hours. M<sub>N</sub> (f) = 25,100 g mol<sup>-1</sup>.

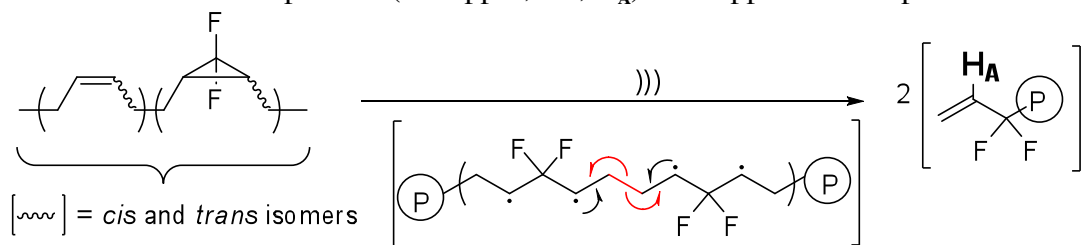


**Figure S82. <sup>1</sup>H NMR spectra obtained before (top, 400 MHz, CDCl<sub>3</sub>) and after [(bottom, 500 MHz, CDCl<sub>3</sub>) 3 hours of sonication of 36 % *c/t-g*DFC-PB.**

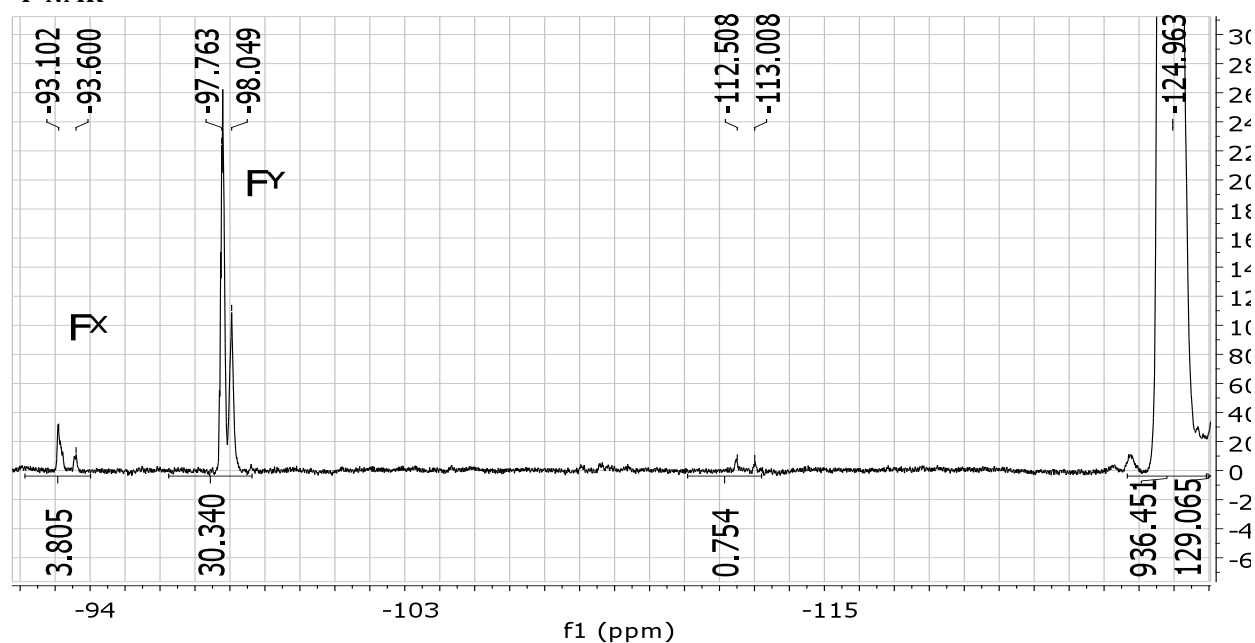


**Figure S83. Zoomed  $^1\text{H}$  spectra after 3 hours of sonication of 36 % *c/t*-gDFC-PB. Inserted product [1] previously reported compound.<sup>1</sup>**

After sonication the molecular weight of the polymer =  $25,100 \text{ g mol}^{-1}$ . From the initial molecular weight, the calculated average number of polymer scission events (scission cycle, SC) =  $[\ln(275,000) - \ln(25,100)] \div \ln(2) = 3.45$ . From each scission, two new end groups are formed. Assuming that each scission event occurs between adjacent, ring opened diradicals, this will result in the formation of 20 new alkenes as a result of the disproportionation as calculated from:  $\# \text{ end groups} = 2 \times [2^{\text{SC}} - 1]$ . The initial polymer is composed of 2436 PB ‘monomers’ and 1376 gDFC ‘monomers’ as calculated from dividing the initial molecular weight of the polymer ( $275,000 \text{ g mol}^{-1}$ ) by the average molecular weight of a monomer unit on the polymer =  $(0.361 \times 104.1) + (0.639 \times 54.09) = 72.14 \text{ g mol}^{-1}$ . Therefore, setting the 1,4-PB alkene resonances (5.41 ppm) to 4872 (2H per ‘monomer’  $\times$  2436) leads to the observed formation of 31 equivalents of new ‘alkene’ product (5.87 ppm, 1H,  $\text{H}_\text{A}$ ) after application of pulsed ultrasound.



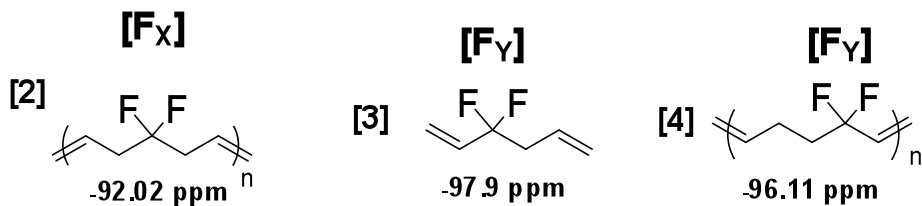


**<sup>19</sup>F-NMR**

**Figure S84. Zoomed region of the <sup>19</sup>F NMR spectra observed after sonication of 36 % *c/t*-gDFC-PB.**

After sonication the change in molecular weight of the polymer indicates that the number of new end groups on the polymer should be ~20 monomers. The initial polymer is composed of 1376 gDFCs, therefore, setting the total integration of <sup>19</sup>F resonances to 2752 (2F per ‘monomer’) leads to  $34.8 \div 2 \text{ F} = 17$  new ‘end group’ difluoro ‘monomers’ after sonication. The number of end groups as a result of *adjacent diradical disproportionation* are thus the resonances at -97.8 ppm, [~15 ‘monomers’] and -93.4 ppm [~2 ‘monomers’]. The total number of new resonances (17) is in excellent agreement with the value calculated (20) assuming all scission events have occurred between adjacent, tension trapped diradicals. By comparison to known compounds [2]<sup>2</sup>, [3]<sup>3</sup>, [4]<sup>2</sup>, we indicate the following product distribution from analysis of the sonicated polymer.

**Reference Compounds**



$^1\text{H}$ - $^1\text{H}$  COSY analysis of sonicated 36 % *g*DFC shows that the newly formed alkene resonance at 5.86 ppm is coupled only to the alkene region, supporting formation of an alkene without neighboring methylene protons along the polymer chain.

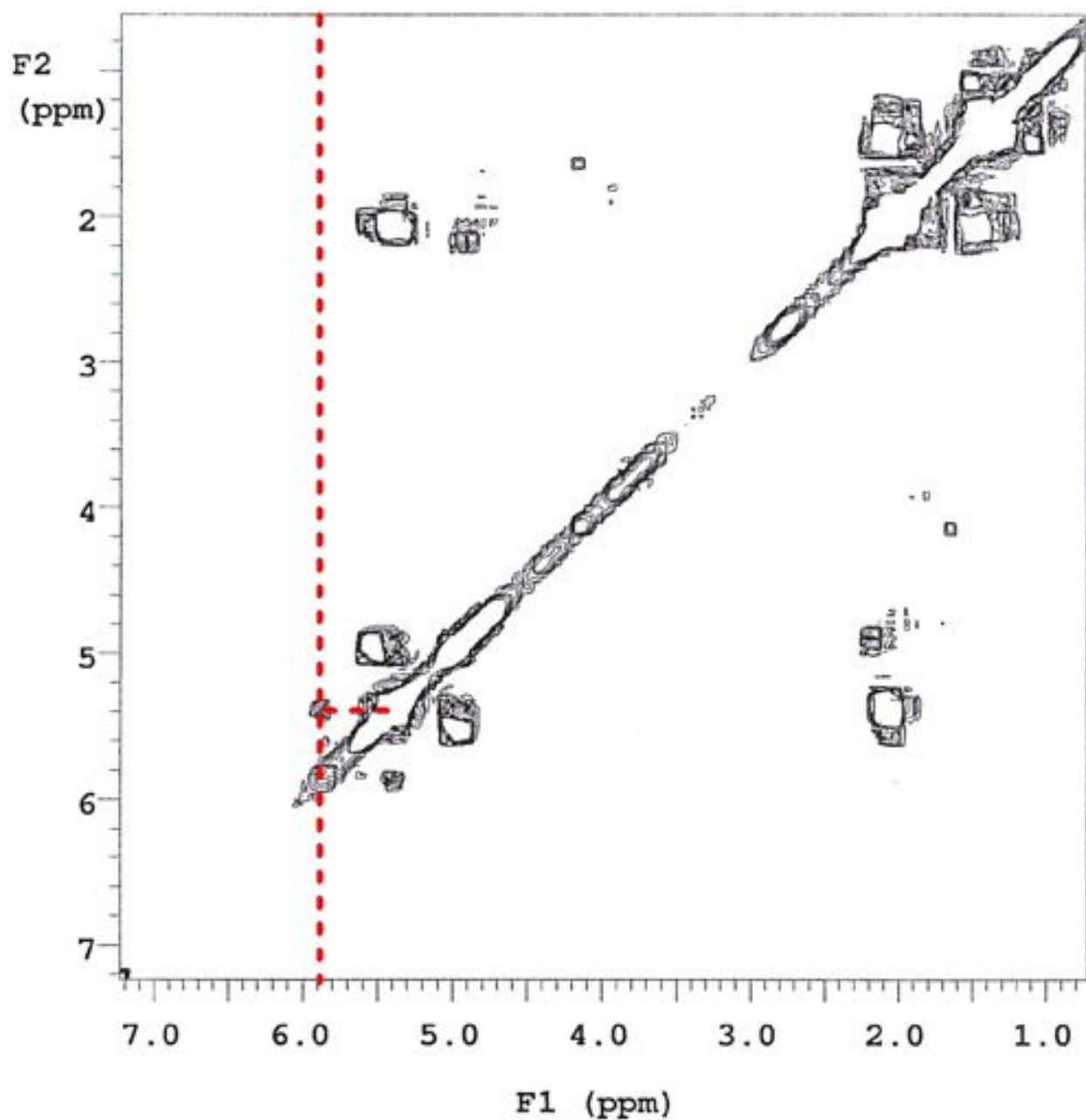


Figure S85. New alkene resonance observed after sonication of 36 % *c/t-g*DFC (5.87 ppm) is only coupled to other alkenes in the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (500 MHz,  $\text{CDCl}_3$ ).

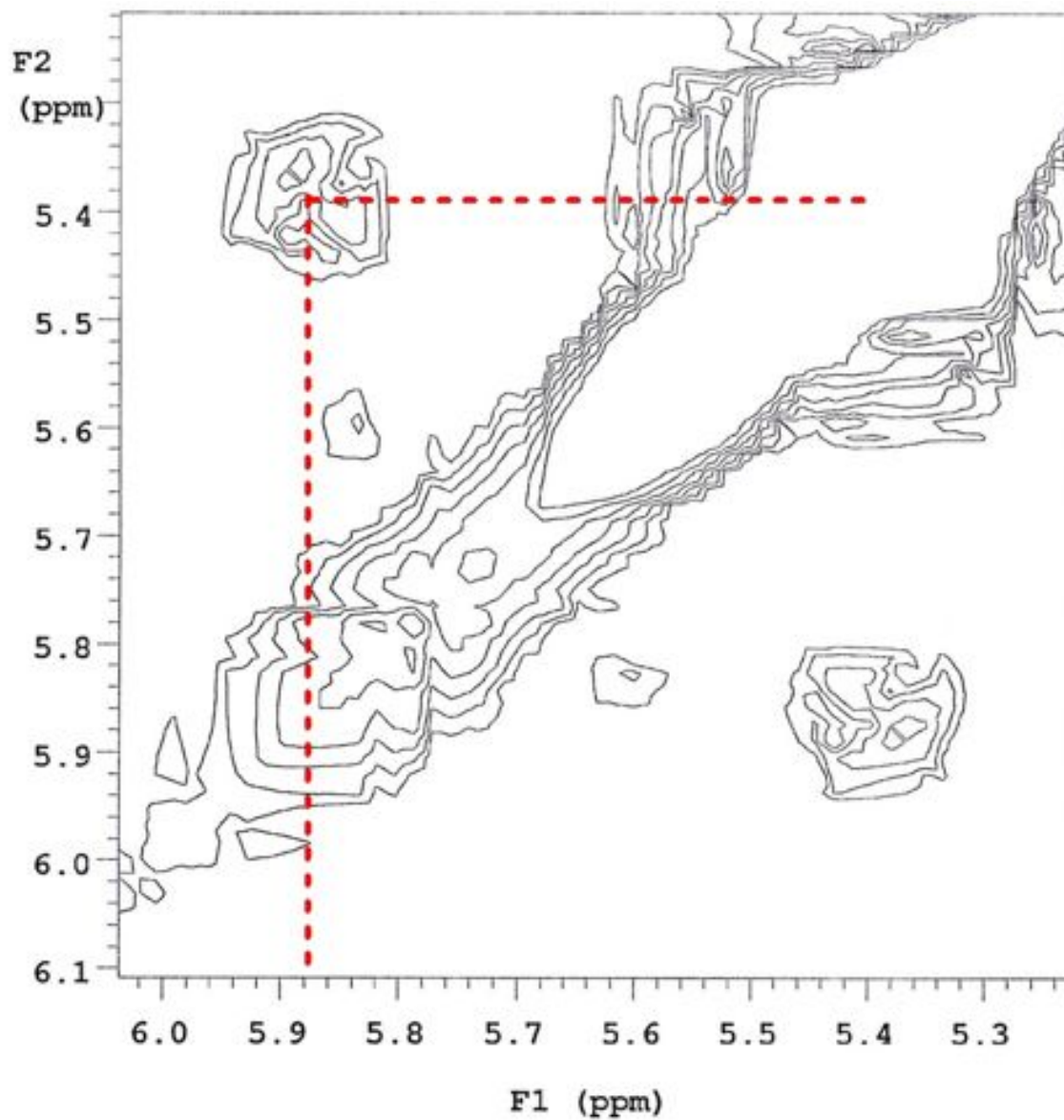
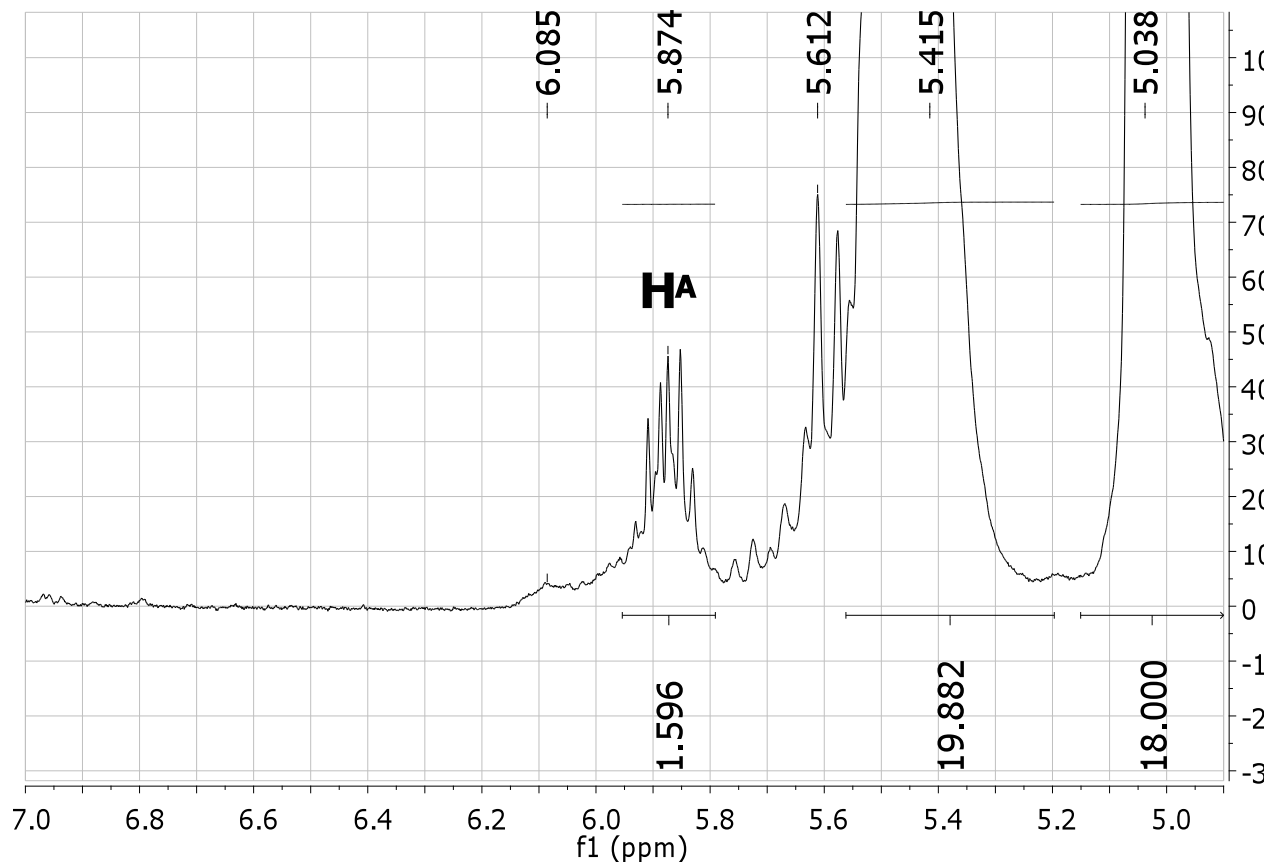


Figure S86. Zoomed region of the  $^1\text{H}$ - $^1\text{H}$  COSY shows that the new alkene resonance observed after sonication of 36 % *c/t*-gDFC (5.87 ppm) is only coupled to other alkenes in the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (500 MHz,  $\text{CDCl}_3$ ).

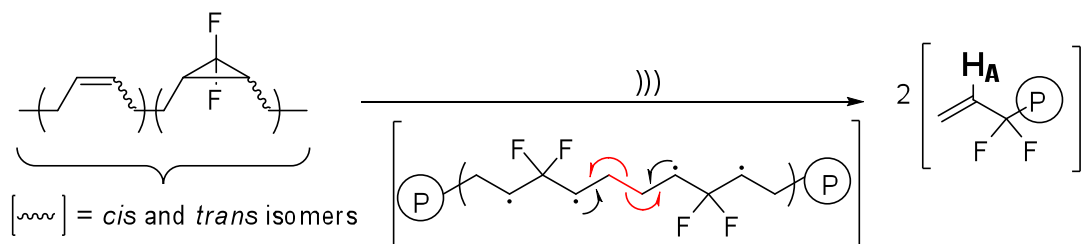
### 177 kDa 95 % *c/t*-gDFC-PB

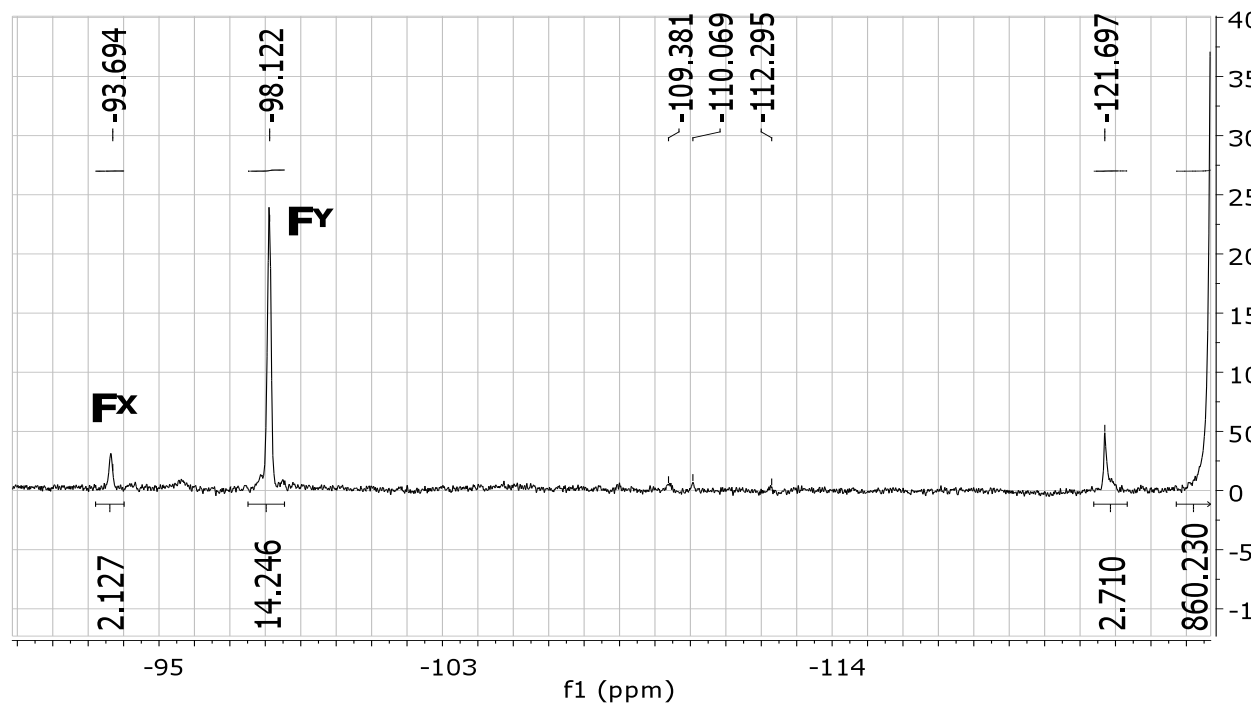
Sonication of 95 % *c/t*-gDFC for 60 minutes after 30 minutes of deoxygenation with bubbling N<sub>2</sub> leads to a polymer  $M_N(f) = 45,000 \text{ g mol}^{-1}$ .



**Figure S87.** Zoomed region of the <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) after sonication of 95 % *c/t*-gDFC-PB.

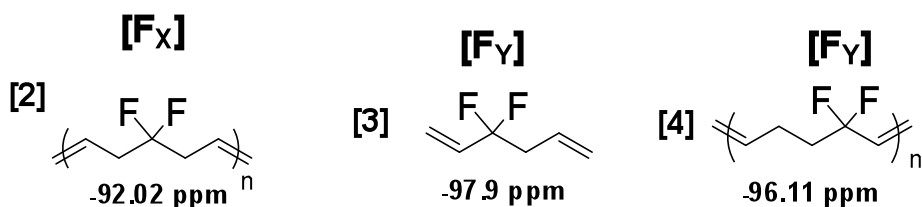
After sonication the molecular weight of the polymer = 45,000 g mol<sup>-1</sup>. Calculating the number of ‘end groups’ formed as a result of polymer scission = 5.9 end groups. The initial polymer is composed of 9 PB and 1732 gDFC ‘monomers’ of which the 9 PB ‘monomers’ are 1,2-vinyl substituents (5.04 ppm – 2H; 5.42 ppm = 1H). Therefore, setting the PB resonance at 5.04 ppm to 18H (2H per PB monomer) leads to formation of 1.6 equivalents of disproportionate end groups at 5.87 ppm (1H, **H<sub>A</sub>**, diradical disproportionation product).





**Figure S88.**  $^{19}\text{F}$  NMR zoomed spectrum (376 MHz,  $\text{CDCl}_3$ ) of 95 % *c/t*-gDFC-PB after sonication.

After polymer sonication (95 % *c/t*-gDFC-PB) the polymer molecular weight is  $45,000 \text{ g mol}^{-1}$ , a calculated number of formed end groups as a result of coupled diradical disproportionation is 5.9. The initial polymer is composed of 1732 gDFC ‘monomers’ and the sum of the integrated spectrum was set to 3464 (2F per monomer). The subsequent number of new  $^{19}\text{F}$  resonances as a result of coupled diradical disproportionation was then calculated as 8.2 from the  $^{19}\text{F}$  NMR spectrum. The formation of products at -93.7 ppm and -98.2 ppm (-122 ppm is from the initial polymer) integrate to a value well correlated with the calculated number of end groups from the change in molecular weight (6).



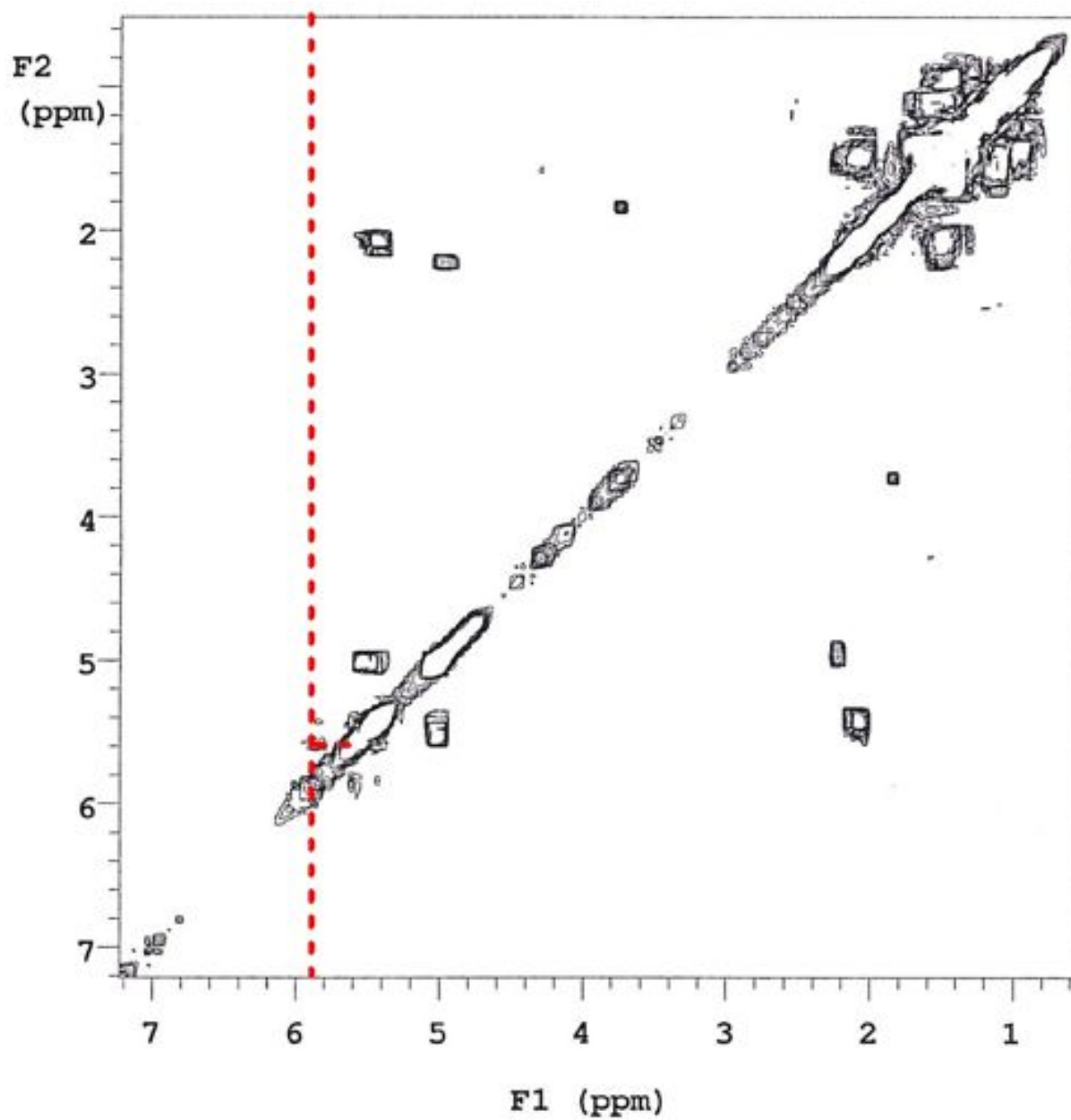


Figure S89. New alkene resonance observed after sonication of 95 % *c/t*-gDFC (5.87 ppm) is only coupled to other alkenes in the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (500 MHz,  $\text{CDCl}_3$ ).

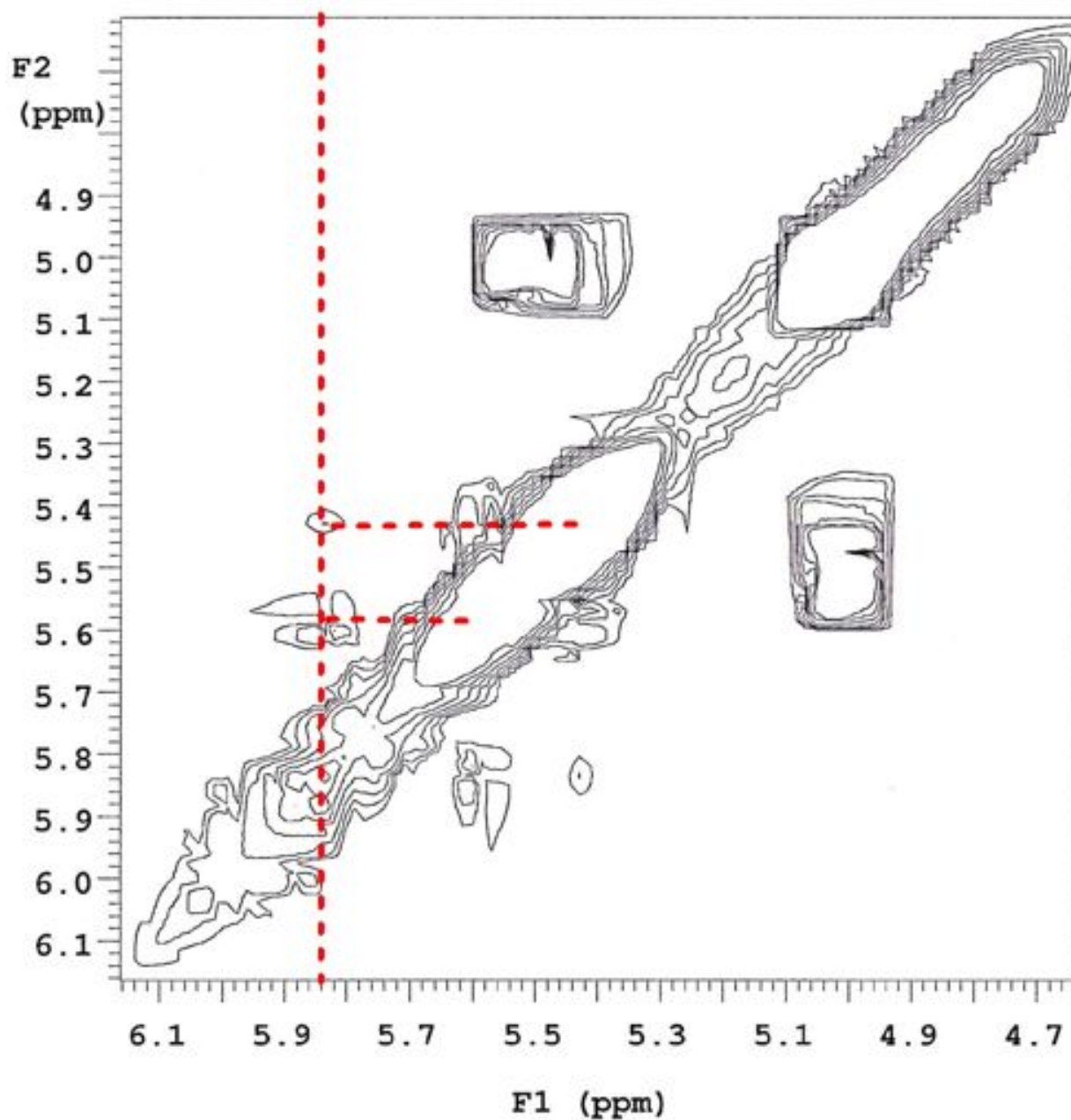
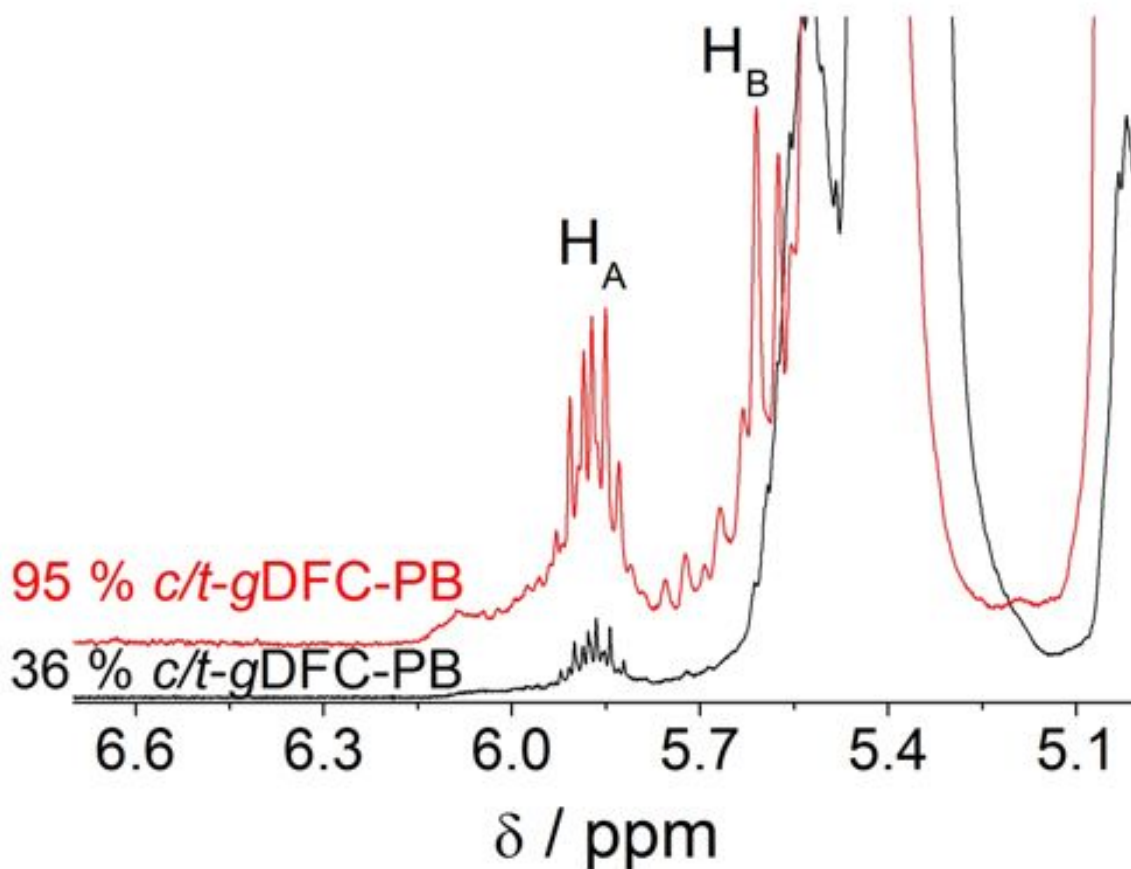


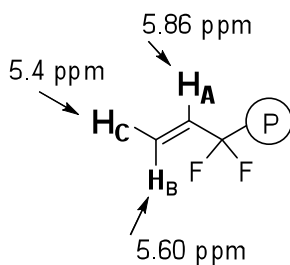
Figure S90. New alkene resonance observed after sonication of 95 % *c/t*-gDFC (5.87 ppm) is only coupled to other alkenes in the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (500 MHz,  $\text{CDCl}_3$ ).

36 % ))) vs. 95 % )))

$^1\text{H}$  NMR

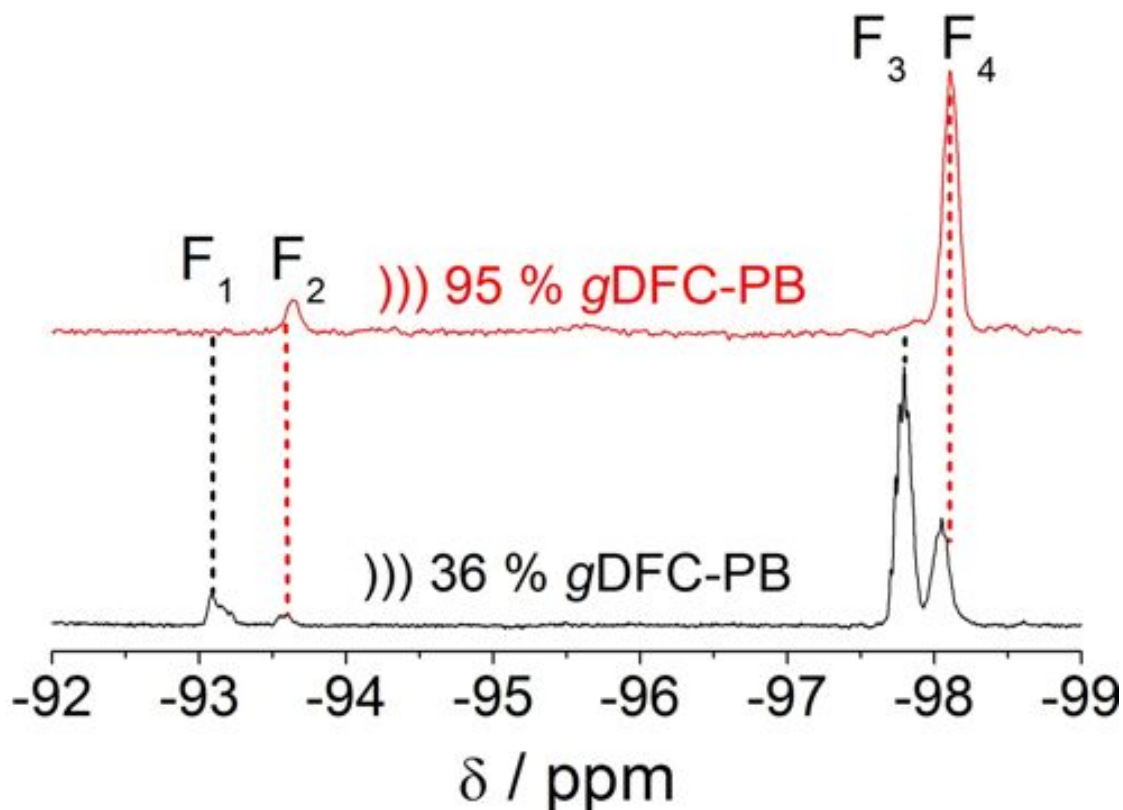


**Figure S91.** A comparison of the  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ ) after sonication of 95 % and 36 % *c/t*-gDFC-PBs indicates the same products are formed from adjacent diradical disproportionation reactions.



**Figure S92.** Combining COSY data with  $^1\text{H}$  NMR spectra allows assignment of  $\text{H}_\text{B}$  while the likely chemical shift of the remaining alkene proton is  $\sim 5.4$  ppm which is not observed in the  $^1\text{H}$  NMR spectrum, but cross-coupling is observed in the  $^1\text{H}$ - $^1\text{H}$  COSY after sonication of 95 % *c/t*-gDFC-PB.





**Figure S93.** Diradical disproportionation products observed by <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) give insights into the microstructure around the disproportionated product.

The sonication of 36 % and 95 % gDFC polymers led to new <sup>19</sup>F-NMR resonances centered at -93.5 ppm and -98 ppm that are consistent with previously reported chemical shifts of known 3,3-difluoroalkene products. The variation in chemical shifts between the two sonicated polymers is likely a result of neighboring monomer repeat unit effects. For example, disproportionated 3,3-difluoroalkene product on the 36 % gDFC polymer may be neighbored by either a PB (-93.1 ppm, -97.8 ppm) or unopened gDFC (-93.6 ppm, -98.0 ppm). These assignments are supported by the fact that end group analysis of sonicated 95 % gDFC polymer is composed of only one set of <sup>19</sup>F-NMR chemical shifts (-93.6 ppm, -98.0 ppm). Both the magnitude of the chemical shifts and the integrated values of the resonances are consistent with formation of 3,3-difluoroalkene products that result from coupled, diradical disproportionation.

**Table of *g*DFC Activation**

RANDOM <i>c/t-g</i> DFC-PBs						
% <i>g</i> DFC	$M_N / \text{g} \cdot \text{mol}^{-1}$	FW	DP	$P_{FF}$	$P^*$	$\phi_1$
3.8	96,800	55.99	1729	0.00144	2.50	.414
8.0	192,000	58.09	3305	0.00640	21.15	.313
9.1	179,000	58.64	3052	0.00828	25.28	.304
10.9	154,000	59.54	2586	0.01188	30.73	.299
22.0	190,000	65.09	2919	0.04840	141.28	.253
32.4	319,000	70.29	4538	0.10498	476.39	.210
36.1	275,000	72.14	3812	0.13032	496.76	.190
47.4	173,000	77.79	2224	0.22468	499.63	.183
51.7	290,000	79.95	3627	0.26729	969.59	.133
58.7	88,400	83.45	1059	0.34457	365.03	.193
95.1	177,000	101.65	1741	0.90440	1574.81	.072
ROMP <i>trans-g</i> DFC-PBs						
% <i>g</i> DFC	$M_N / \text{g} \cdot \text{mol}^{-1}$	FW	DP	$P_{FF}$	$P^*$	$\phi_1$
33.3	65,500	70.74	926	0	0.000	.468
66.7	66,200	87.45	757	0.667	504.941	.183

Table S1: List of sonicated *g*DFC-PBs and values reported in the main text.

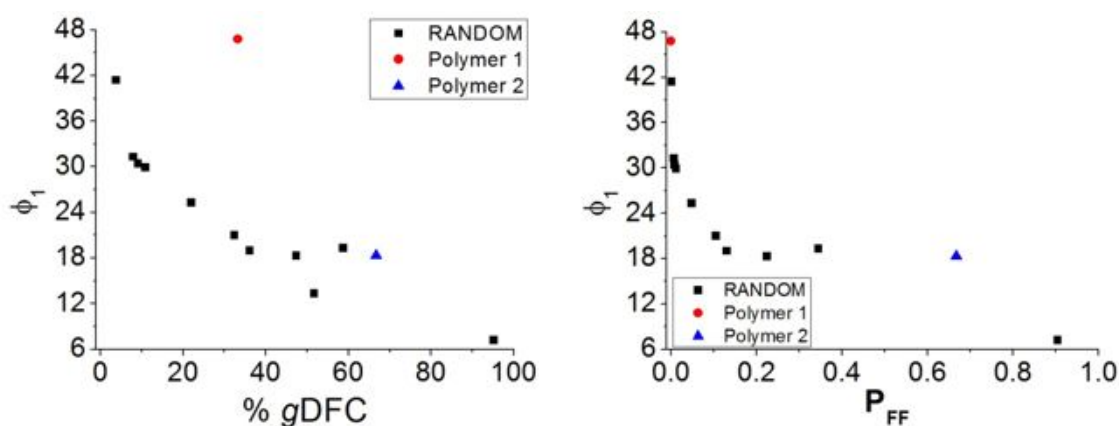


Figure S94: Plots of isomerization versus *g*DFC loading (left) and  $P_{FF}$  (right) are incomplete comparisons in the activation of *trans-g*DFCs on *g*DFC-PB copolymers.

## Computational Work

### Theory

We have used the *ab initio* steered molecular dynamics method (AI-SMD)<sup>4</sup> to examine the effects of a mechanical force on a *gem*-difluorocyclopropane (gDFC) dimer where one gDFC is in the *cis* conformation while the other is in the *trans* conformation. The potential energy surface and the internal forces were calculated “on the fly” by solving the electronic Schrödinger equation, which allows for arbitrary bond rearrangement. An external force is added to the *ab initio* internal forces and acts only on the atoms that are being pulled, which we refer to as “attachment points” (APs). Thus, the total force is then given as the vector sum of the *ab initio* internal forces and the external force:

$$\mathbf{F}^{tot} = \mathbf{F}^{ab\ initio} + \mathbf{F}^{ext} \quad [1]$$

Once the total force is calculated, the position and momentum of all the atoms are then propagated according to classical equations of motion. We have chosen to define the external force using a “constant force fixed pulling” scheme where a constant magnitude force ( $F_0$ ) is applied to each AP and pulls it toward a corresponding fixed point, which we call a “pulling point” (PP). The expression for the external force is then given by:

$$\mathbf{F}_{ext} = \sum_i^{N_{attach}} F_0 \mathbf{n}_i \quad [2]$$

The pulling direction ( $\mathbf{n}_i$ ) for each attachment point is defined as:

$$\mathbf{n}_i = \frac{\mathbf{R}_i^{fix} - \mathbf{R}_i}{\|\mathbf{R}_i^{fix} - \mathbf{R}_i\|} \quad [3]$$

where  $\mathbf{R}_i^{fix}$  and  $\mathbf{R}_i$  represent the positions of the  $i$ th fixed point and corresponding attachment point, respectively. Using this framework, the potential energy is adjusted so that it agrees with the AI-SMD forces defined above. The expression for this *force-modified* potential energy surface (FMPES) is:

$$V_{total}(\mathbf{R}) = V_{ab\ initio} + F_0 \sum_i^{N_{attach}} (\|\mathbf{R}_i^{fix} - \mathbf{R}_i\| - \|\mathbf{R}_i^{fix} - \mathbf{R}_i^0\|) \quad [4]$$

where  $\mathbf{R}_i^0$  is the initial position of the attachment points.

### Simulation Details

All calculations were done using the MOLPRO software package<sup>5</sup> within a modified version of the *ab initio* multiple spawning (AIMS)<sup>6-8</sup> molecular dynamics code. The electronic structure was solved using the complete active space self-consistent field (CASSCF) method<sup>9</sup> and a 6-31G basis set. An active space of four electrons in four orbitals was selected, i.e. CAS(4/4). The four orbitals correspond to the  $\sigma$  and  $\sigma^*$  orbitals of the distal C-C single bond relative to the  $\text{CF}_2$  group for each gDFC. Simulations were followed for 1ps with an integration time step of 0.5fs. Initial conditions for the position and momentum were randomly sampled from a finite temperature Wigner distribution at 280K constructed from CAS(4/4)/6-31G

vibrational frequencies at the no-force minimum geometry. Modes with frequencies under  $150\text{cm}^{-1}$  were ignored when generating this distribution since the harmonic approximation is poor for such low frequency modes.

### Supplementary AI-SMD Results

As mentioned in the main text, we ran a total of 20 trajectories at a force of  $3\text{nN}$  on a (*cis*, *trans*) gDFC dimer. Two of the trajectories showed scission of the central C-C bond between the gDFC mechanophores after adjacent diradicals had already been formed. However, the dominant mechanism observed in the simulations was irreversible ring opening of the gDFCs to form adjacent diradicals. In Figure S84a, we show snapshots of a representative trajectory where only ring opening of the gDFCs occurred.

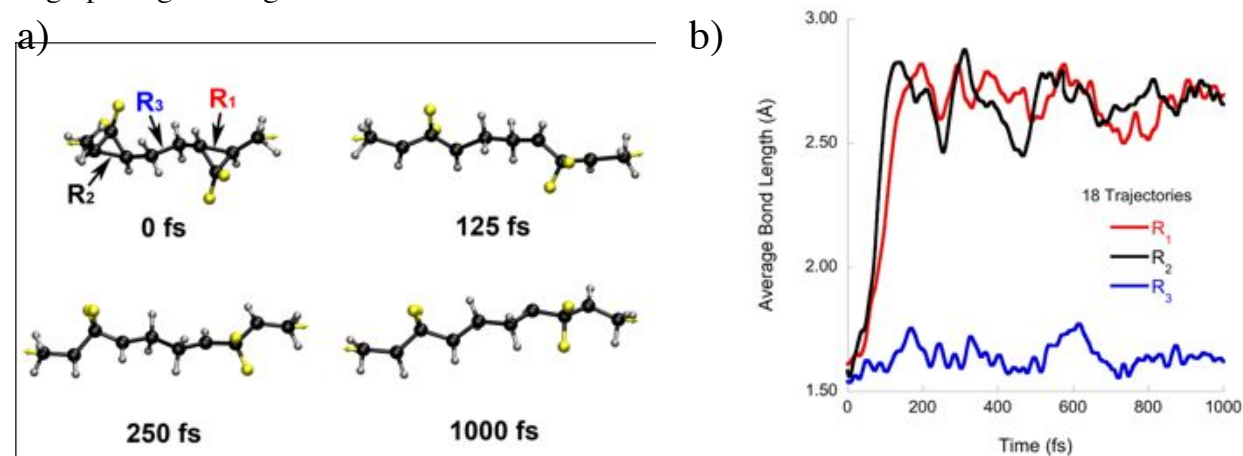


Figure S84. (a) Snapshots of a representative trajectory indicating ring opening of the gDFCs to form adjacent diradicals while the C-C central bond remains in tact. AI-SMD simulations indicate 18 out of 20 trajectories give this outcome. (b) Average bond lengths associated with gDFC ring opening and bond scission as a function of time for these 18 trajectories.

In total, 18 out of 20 trajectories resulted in this outcome. In Figure S84b, we plot the average bond length of the distal C-C bond relative to the  $\text{CF}_2$  group for each gDFC ( $R_1$  and  $R_2$ ) and the central C-C bond ( $R_3$ ) for these 18 trajectories. We can clearly see that ring opening occurs to the diradical for both gDFCs, but the C-C central bond remains in tact. Even though two trajectories showed fragmentation along the C-C central bond, ring opening of both gDFCs to form adjacent diradicals is the predominant mechanism as predicted by AI-SMD simulations.

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