

Supporting Information

**Dual-Site Catalysis for Sustainable Commodity Polymers – Carbonylative  
Copolymerization of Ethylene, Ethylene Oxide, and Tetrahydrofuran**

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1. General methods
2. Comparison of  $^1\text{H}$  NMR spectra of a CO-ethylene-EO-THF tetrapolymer, a CO-ethylene copolymer, a CO-EO-THF terpolymer, and a CO-ethylene-EO-THF- $\text{d}_8$  tetrapolymer.
3.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of the tetrapolymer product
4.  $M_w$  Change over time in HFIPA detected by SLS
5. SLS Zimm plots of the tetrapolymer polymers
6. DSC traces of all samples

## 1. Experimental methods

All manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques. Solvents were purchased from Sigma Aldrich and dried using an MBraun solvent purification system. All other chemicals were purchased from Sigma Aldrich or VWR. THF was further dried over Na/K alloy, vacuum-transferred into a dried storage tube, and kept under N<sub>2</sub>. Ethylene oxide was dried with <sup>n</sup>BuLi, vacuum-transferred into a dried storage tube, and kept under N<sub>2</sub>.

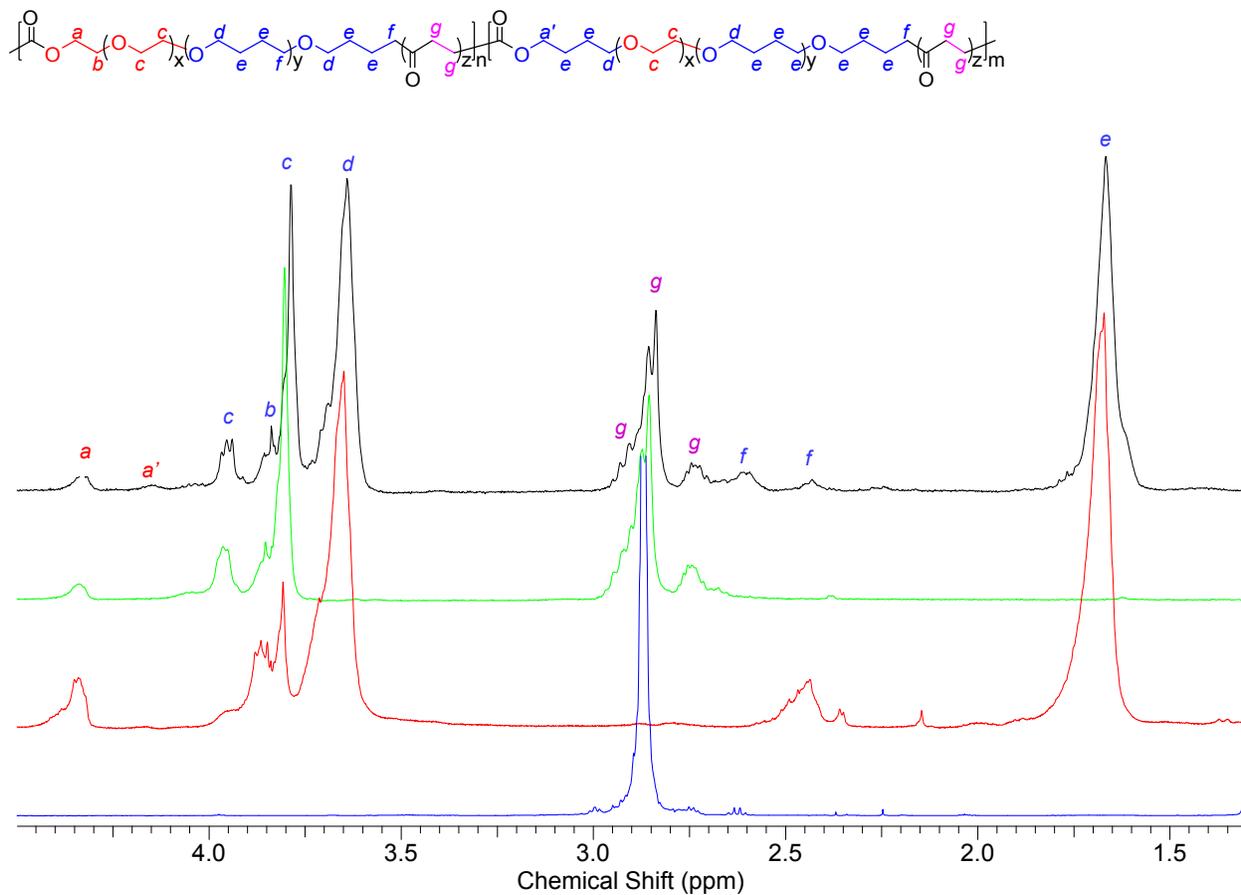
<sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer or a Varian NMRS 500 MHz spectrometer. Chemical shifts were determined using solvent peaks as references for <sup>1</sup>H NMR.

Static light scattering (SLS) measurements were performed on a Brookhaven Instruments light scattering spectrometer equipped with a diode-pumped solid-state (DPSS) laser operating at 633 nm and a BI-9000AT multichannel digital correlator. The polymer solutions were filtered through PTFE syringe filters and loaded into 20 mL vials. Typically, 4 different concentrations (10.0, 7.5, 5.0 and 2.5 g/L except for entry 6. See Figure ) of tetrapolymer and every 2 degree in the angle range from 40° to 120° were used. Refractive index increment ( $dn/dc$ ) was measured using a Brookhaven BI-DNDC differential refractometer instrument. The molecular weights were determined by Zimm plot using Brookhaven light scattering software.

Polymerization was carried out in a 125-mL Parr reactor. The catalyst (15 mg) was loaded in the reactor in the glovebox. The reactor was connected to the Schlenk line, evacuated, and backfilled with CO (1 atm). EO and THF cooled in an ice bath were injected into the reactor under a gentle CO flow in the fume hood. The reactor was pressurized with ethylene and CO and sealed. The reaction was stirred with a magnetic stir bar except for entries 8 and 9 of Table 1.

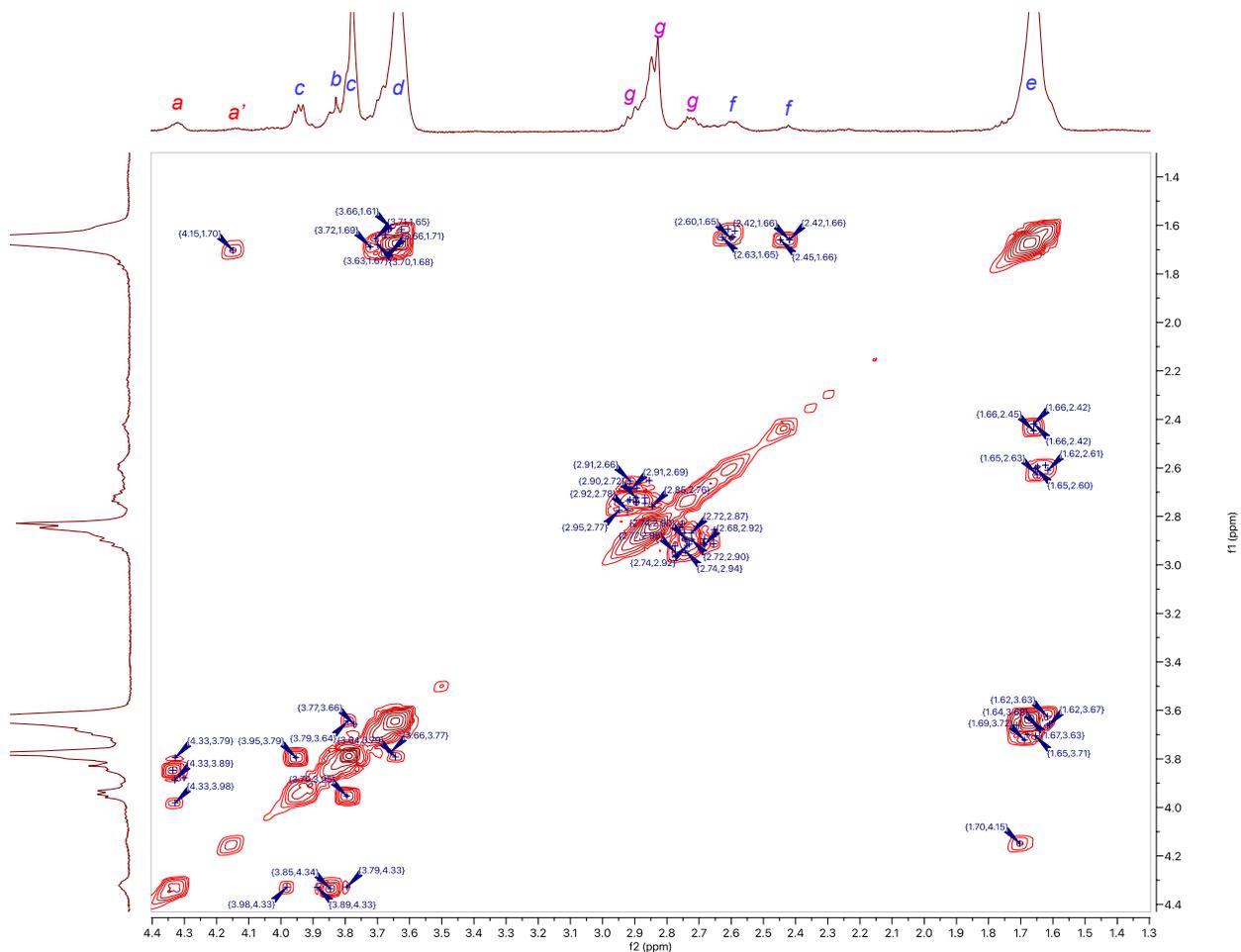
Tensile test was performed on an Instron Model 5567 equipped with a 1000 N load cell. The sample was cut into pieces with an ASTM D638 type V dumbbell die. The tensile bars were held in two clamps with 15 mm gap and extended as a rate of 50 mm/min at room temperature until failure. Strain was measured with an extensometer.

**2. Comparison of  $^1\text{H}$  NMR spectra of a CO-ethylene-EO-THF tetrapolymer, a CO-ethylene copolymer, a CO-EO-THF terpolymer, and a CO-ethylene-EO-THF- $\text{d}_8$  tetrapolymer.**



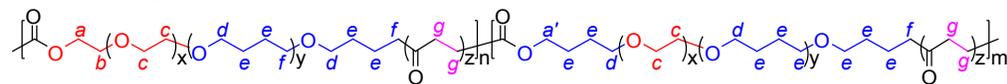
**Figure S1.**  $^1\text{H}$  NMR spectra of tetrapolymer from entry 3 of Table 1 (black), the same tetrapolymer except that THF- $\text{d}_8$  was used instead of THF (green), a non-alternating CO-EO-THF terpolymer (red), and an alternating CO-ethylene copolymer (blue).

### 3. $^1\text{H}$ - $^1\text{H}$ COSY NMR spectrum of the tetrapolymer



**Figure S2.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of the product of COP of cyclic ether and ethylene from Entry 3, Table 1.

Correlated pairs detected:



$a - b$ ,

$a' - e$ ,

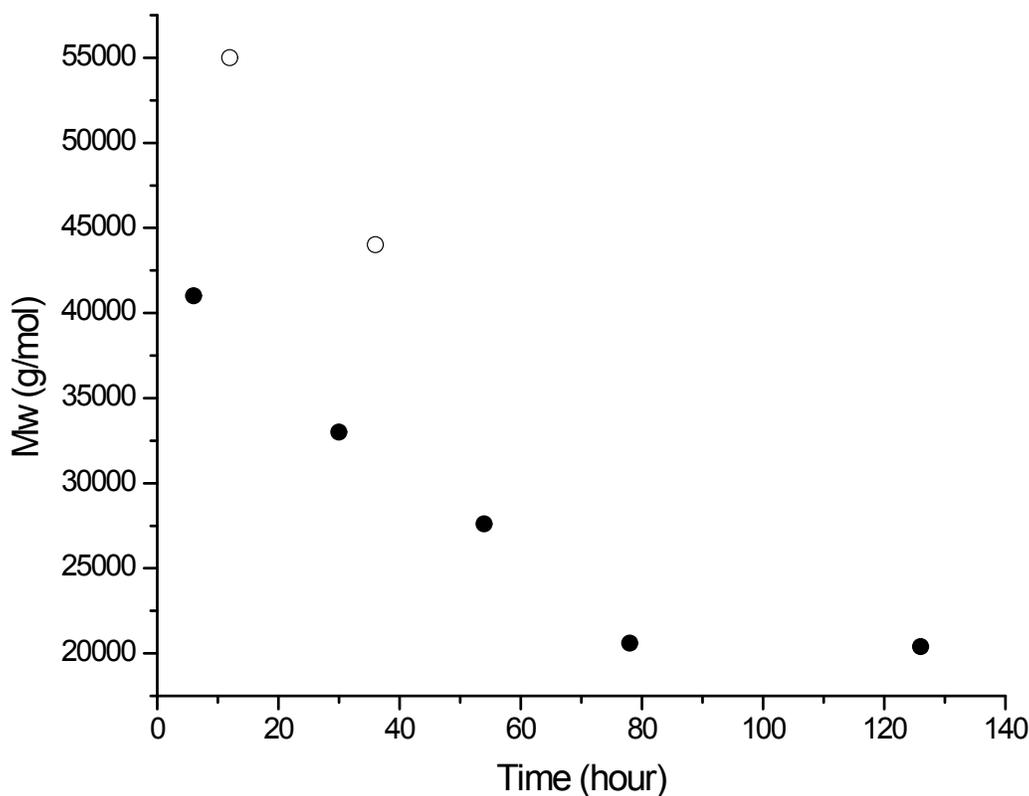
$d - e$ ,

$f - e$ ,

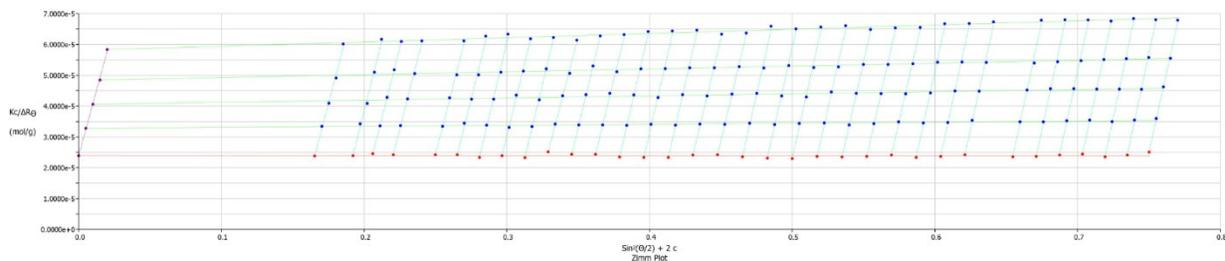
$g$  at 2.92 ppm -  $g$  at 2.75 ppm.

#### 4. $M_w$ Change over time in HFIPA detected by SLS

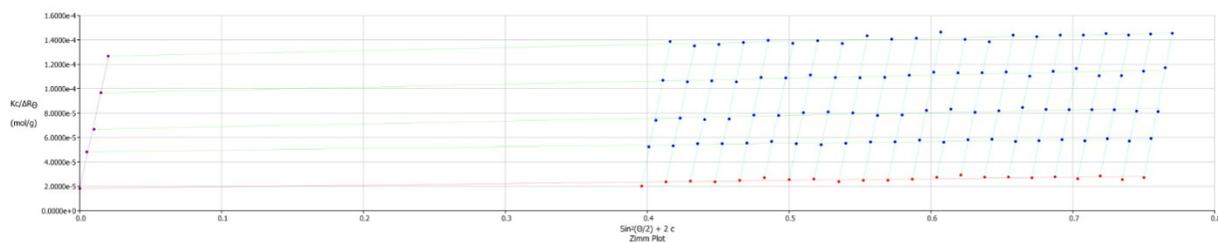
$M_w$  of the product from entry 9, Table 1 was measured at various times after it dissolved in “wet” HFIPA and HFIPA dried with 4 Å molecular sieves for 2 days. The first data point was measured as early as possible after the sample completely dissolved. The dissolution process was noticeably slower in anhydrous HFIPA than in “wet” HFIPA (6 h vs 8 h). Zimm plots corresponding to the data points in Figure S3 are shown in Figures S4 – S10. Refractive index increments were measured on the first day only and used for all subsequent  $M_w$  determinations.



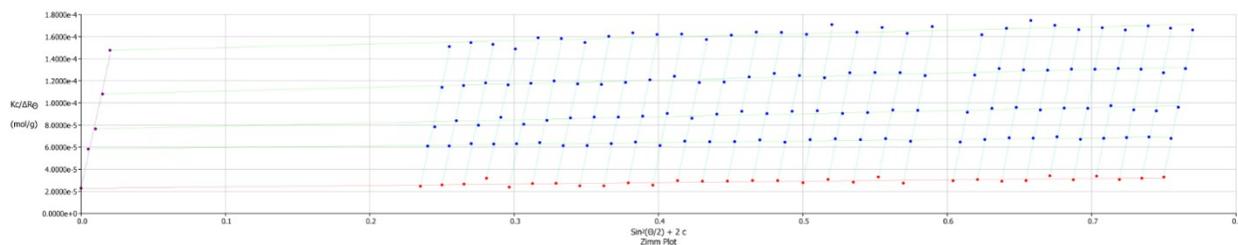
**Figure S3.** Change of  $M_w$  over time for the product from entry 9, Table 1 in “wet” HFIPA (solid circle) and anhydrous HFIPA (open circle).



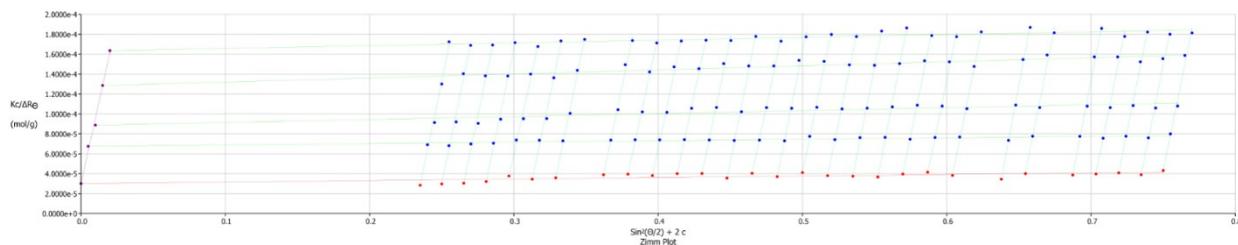
**Figure S4.** Zimm plot of data measured immediately after the samples dissolved in anhydrous HFIPA, corresponding to the first open circle in Figure S3.  $dn/dc = 0.229$  mL/g.



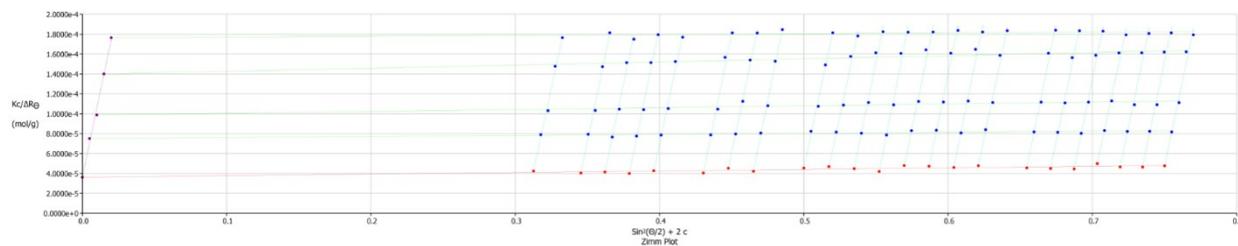
**Figure S5.** Zimm plot of data measured 36 h after the samples were dissolved in anhydrous HFIPA.  $dn/dc = 0.229$  mL/g.



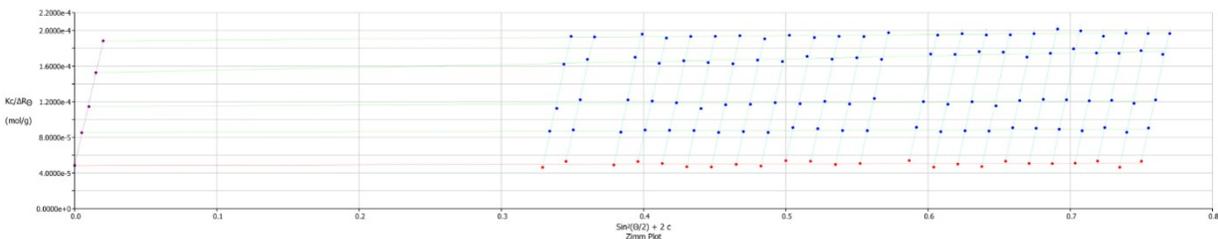
**Figure S6.** Zimm plot of data measured immediately after the samples dissolved in “wet” HFIPA, corresponding to the first solid circle in Figure S3.  $dn/dc = 0.226$  mL/g.



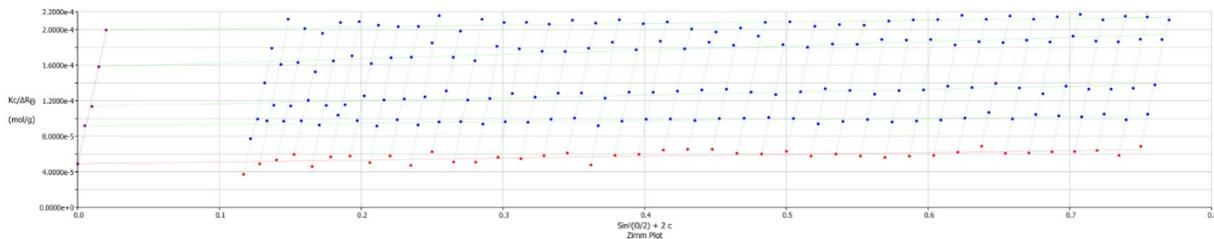
**Figure S7.** Zimm plot of data measured 24 h after the samples dissolved in “wet” HFIPA.  $dn/dc = 0.226$  mL/g.



**Figure S9.** Zimm plot of data measured 48 h after the samples dissolved in “wet” HFIPA.  $dn/dc = 0.226 \text{ mL/g}$ .



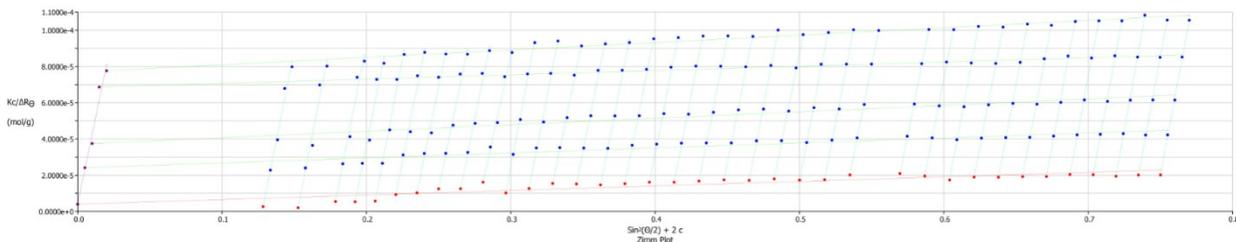
**Figure S9.** Zimm plot of data measured 72 h after the samples dissolved in “wet” HFIPA.  $dn/dc = 0.226 \text{ mL/g}$ .



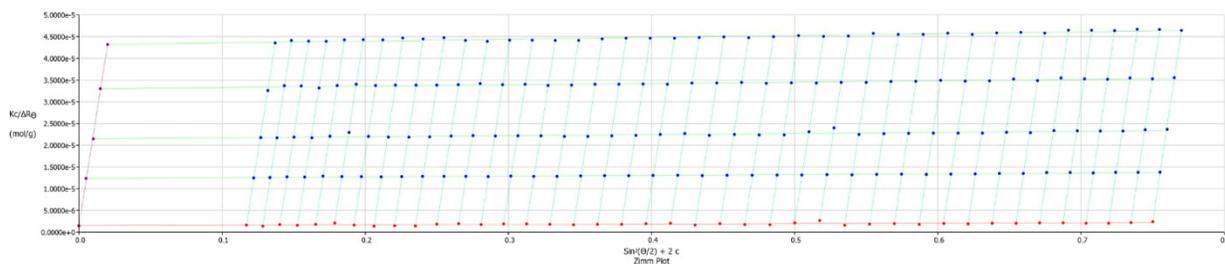
**Figure S10.** Zimm plot of data measured 120 hours after the samples dissolved in “wet” HFIPA.  $dn/dc = 0.226 \text{ mL/g}$ .

## 5. Zimm plots and refractive index increment of the products

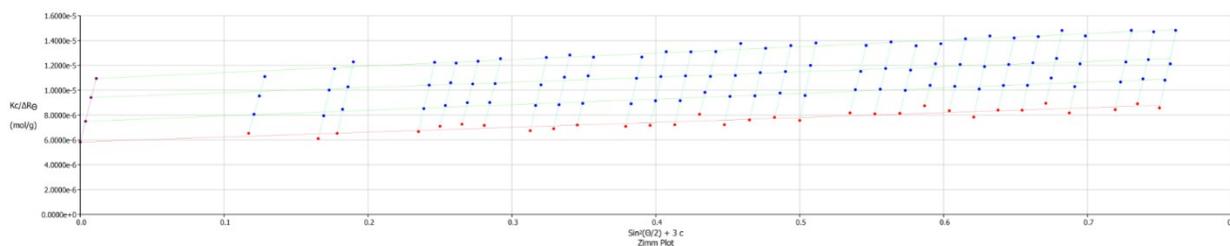
Anhydrous HFIPA was used for the SLS and  $dn/dc$  measurements. Zimm plots are shown below.



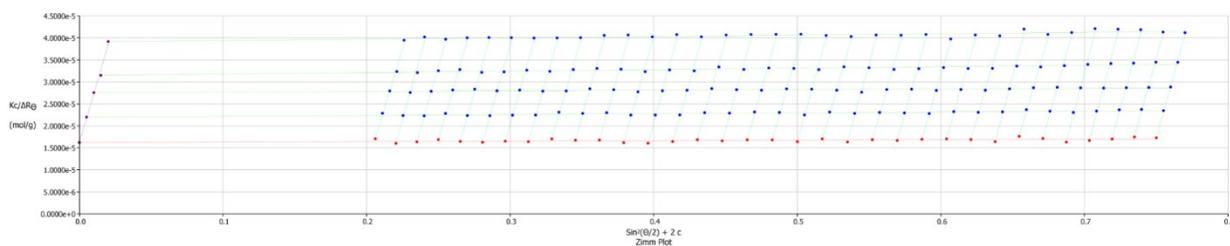
**Figure S11.** Zimm plot of the product from entry 1, Table 1.  $dn/dc = 0.197 \text{ mL/g}$ .



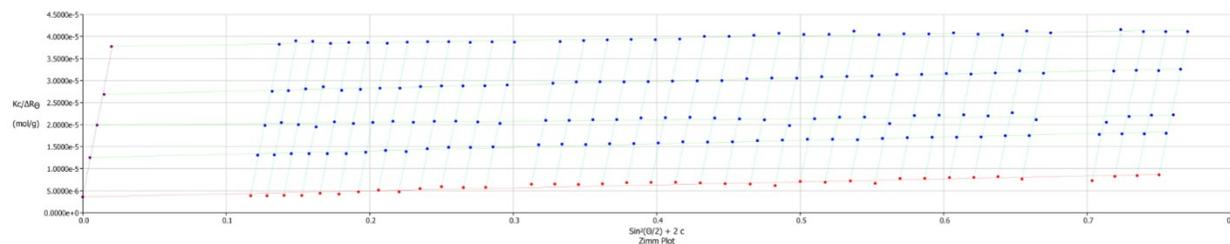
**Figure S12.** Zimm plot of the product from entry 2, Table 1.  $dn/dc = 0.205$  mL/g.



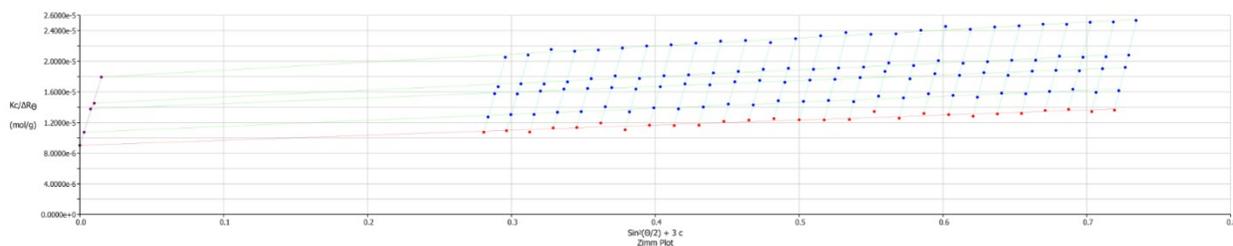
**Figure S13.** Zimm plot of the product from entry 3, Table 1.  $dn/dc = 0.224$  mL/g.



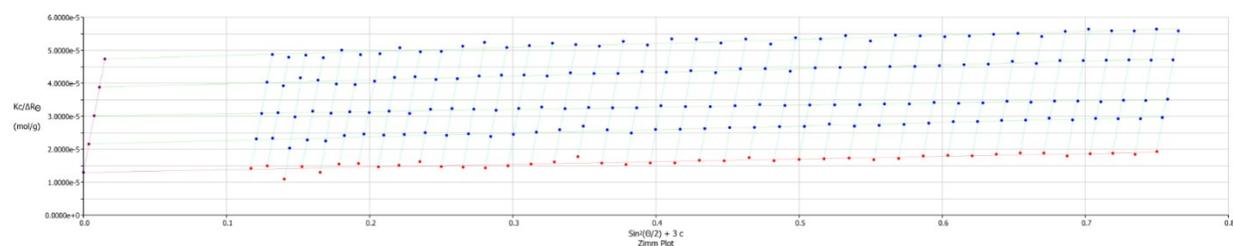
**Figure S14.** Zimm plot of the product from entry 4, Table 1.  $dn/dc = 0.189$  mL/g.



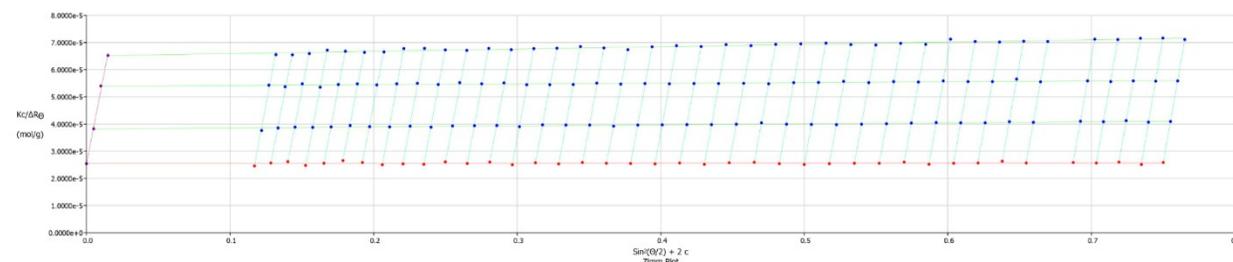
**Figure S15.** Zimm plot of the product from entry 5, Table 1.  $dn/dc = 0.196$  mL/g.



**Figure S16.** Zimm plot of the product from entry 6, Table 1. The concentrations of the solutions were 5, 3.5, 2.5 and 1 g/L, lower than the concentrations of the rest of the experiments. The solutions were sonicated to completely dissolve the samples. This is because the elastomer with a high molecular weight and a high polyether content is difficult to dissolve in HFIPA.  $dn/dc = 0.224$  mL/g.



**Figure S17.** Zimm plot of the product from entry 7, Table 1.  $dn/dc = 0.224$  mL/g.



**Figure S18.** Zimm plot of the product from entry 8, Table 1.  $dn/dc = 0.187$  mL/g.



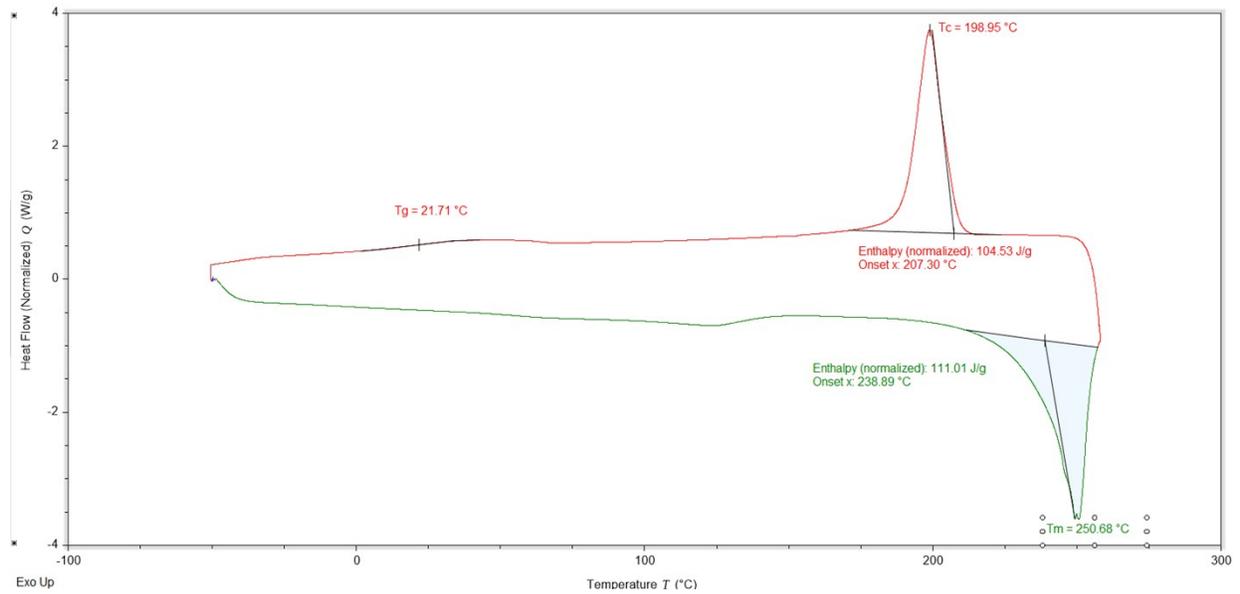
**Figure S19.** Zimm plot of the product from entry 9, Table 1.  $dn/dc = 0.229$  mL/g.

## 6. DSC of samples from entries 8 and 9.

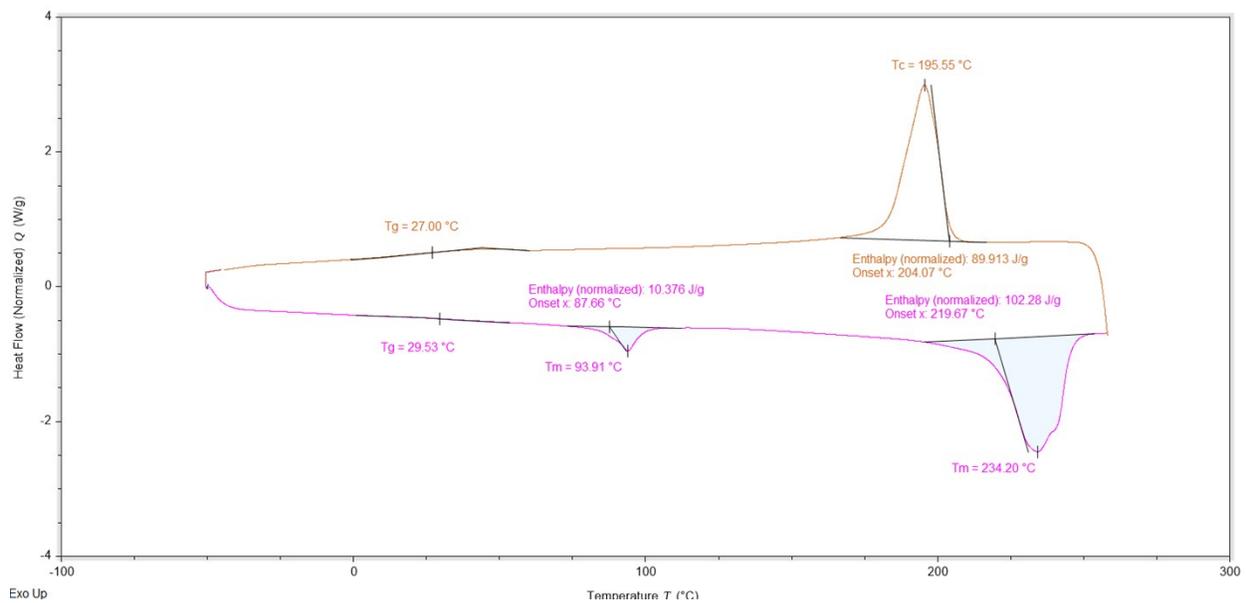
Differential scanning calorimetry (DSC) experiments were performed on a TA Discovery DSC 250 differential scanning calorimeter under nitrogen. Each sample was prepared in a hermetic aluminum pan for experiments with about 5 mg in weight. Temperature was equilibrated to  $-50\text{ }^{\circ}\text{C}$  first, and then the system was isothermal at  $-50\text{ }^{\circ}\text{C}$  for 3 minutes before experiments. The heating rate and cooling rate were  $20\text{ }^{\circ}\text{C}$  per minute. The temperature ranged from  $-50\text{ }^{\circ}\text{C}$  to  $260\text{ }^{\circ}\text{C}$ .

### Entry 1

#### First Cycle

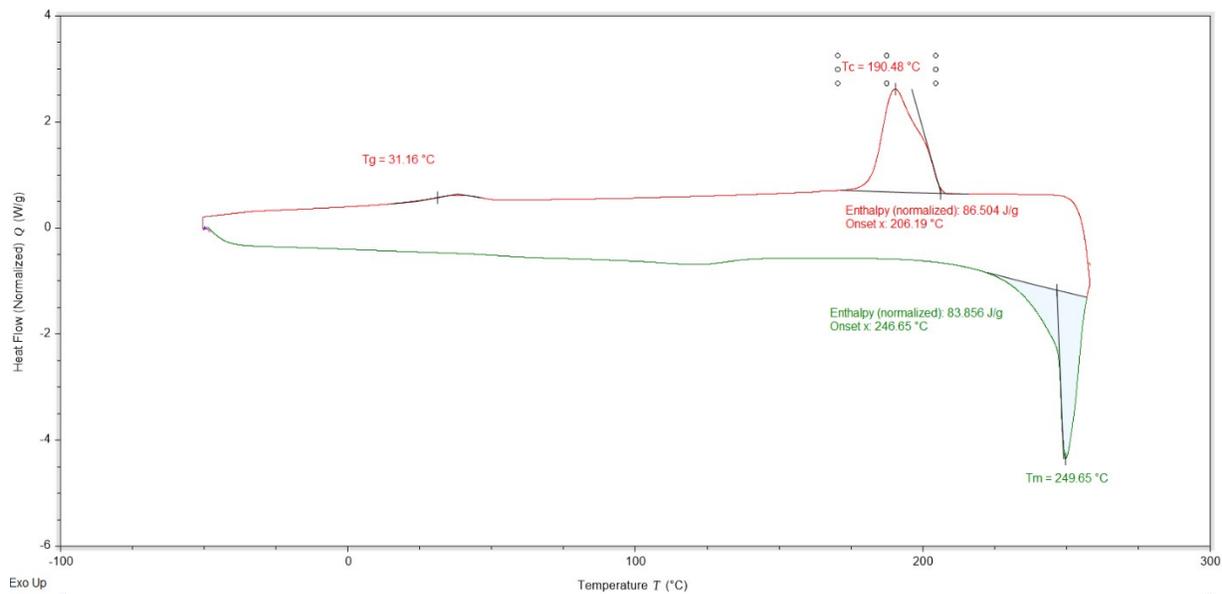


#### Second Cycle

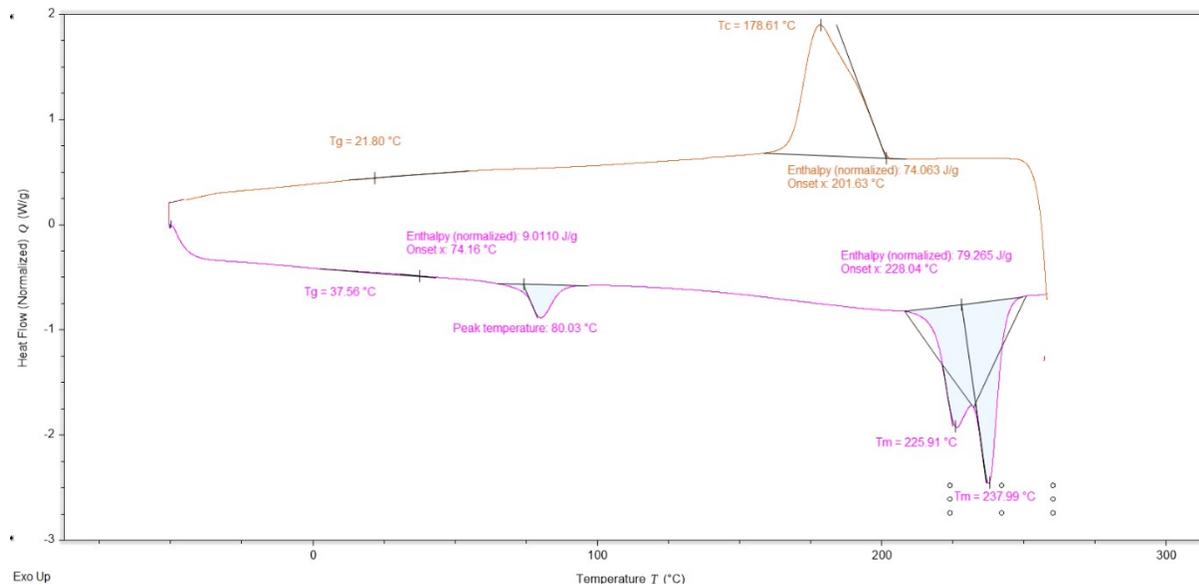


## Entry 2

### First Cycle

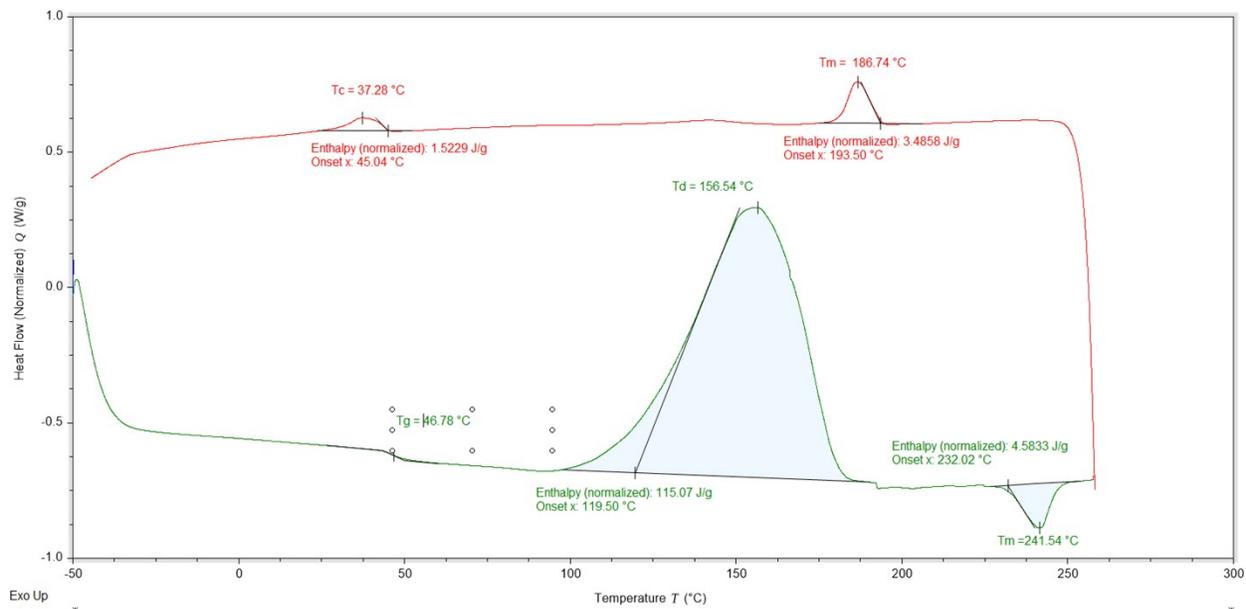


### Second Cycle



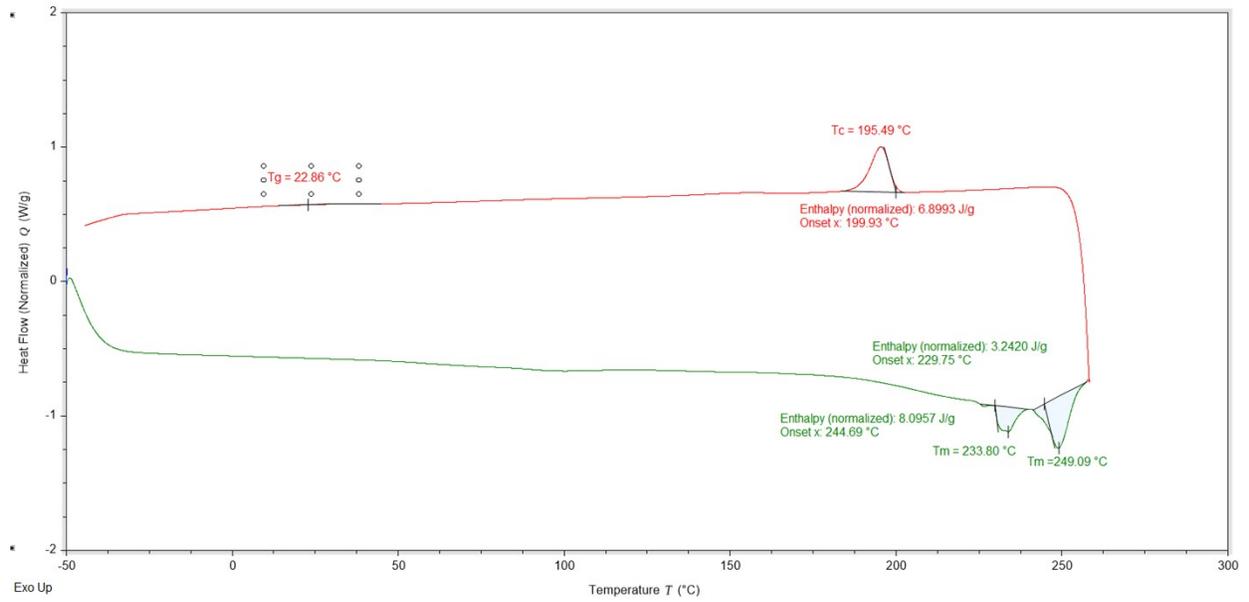
### Entry 3

### First Cycle

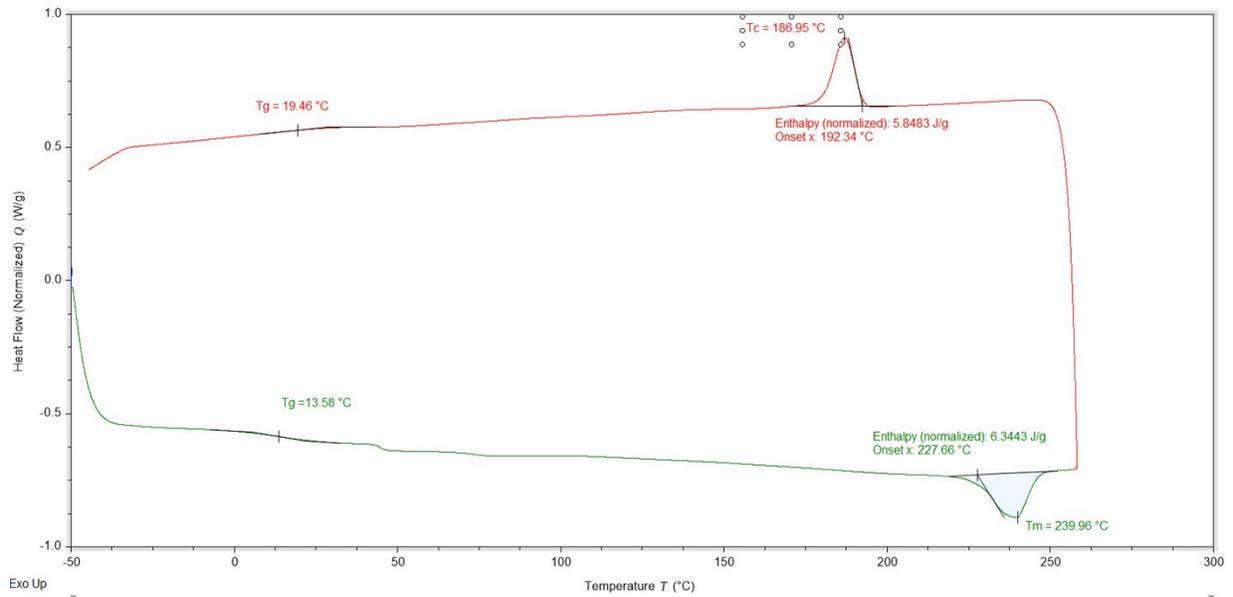


# Entry 4

## First Cycle

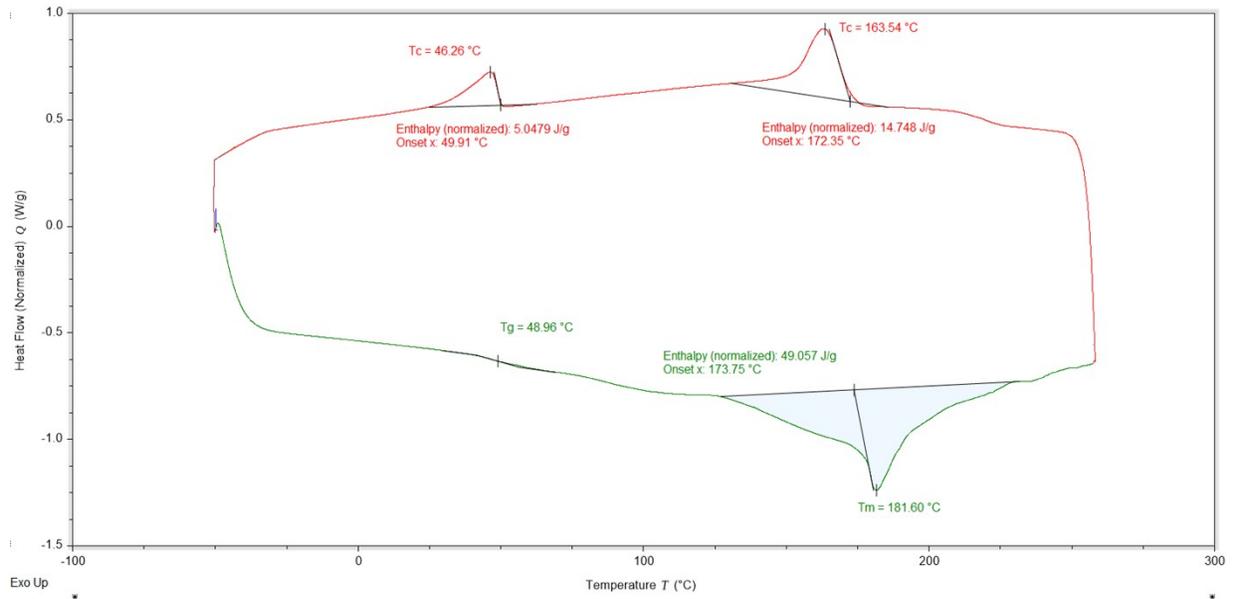


## Second Cycle

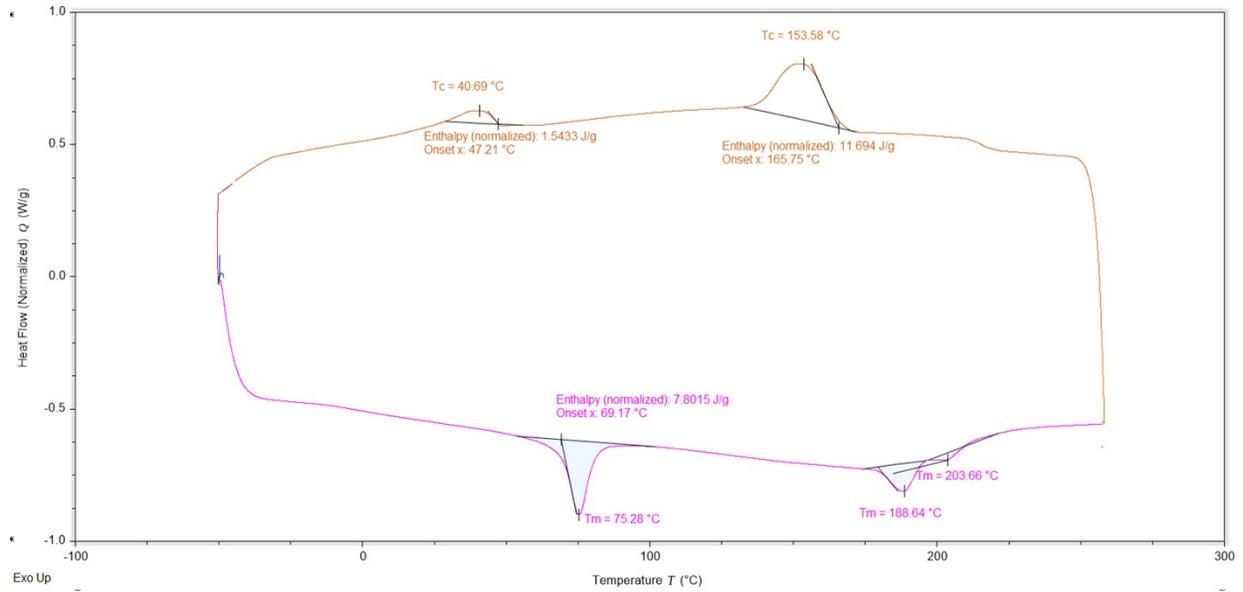


# Entry 5

## First Cycle

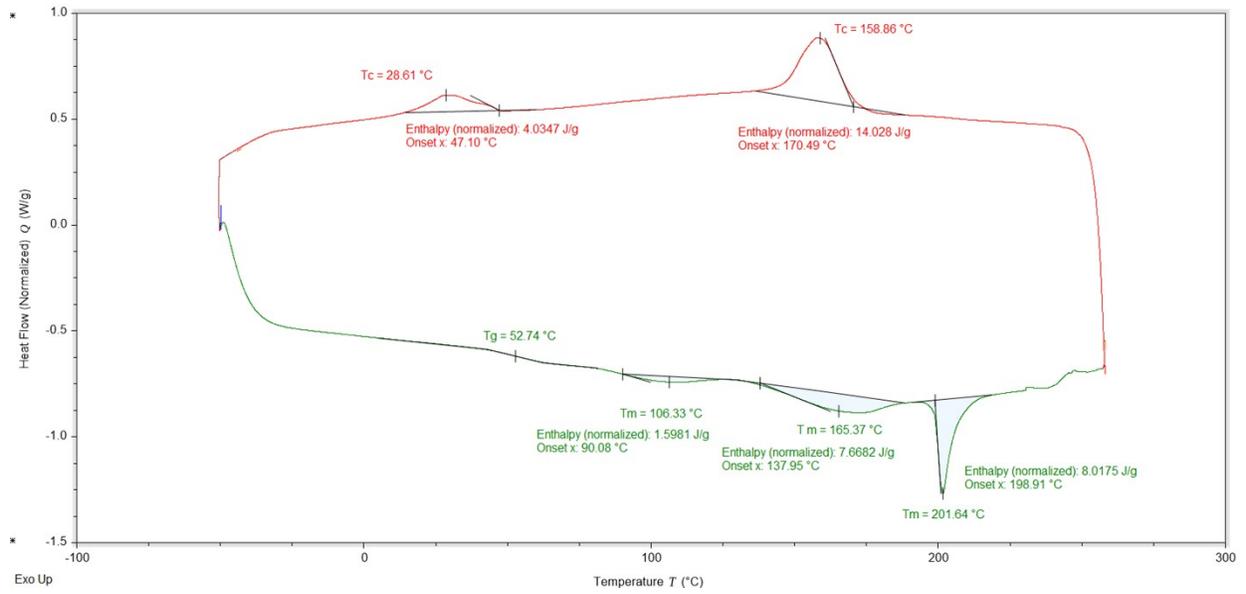


## Second Cycle

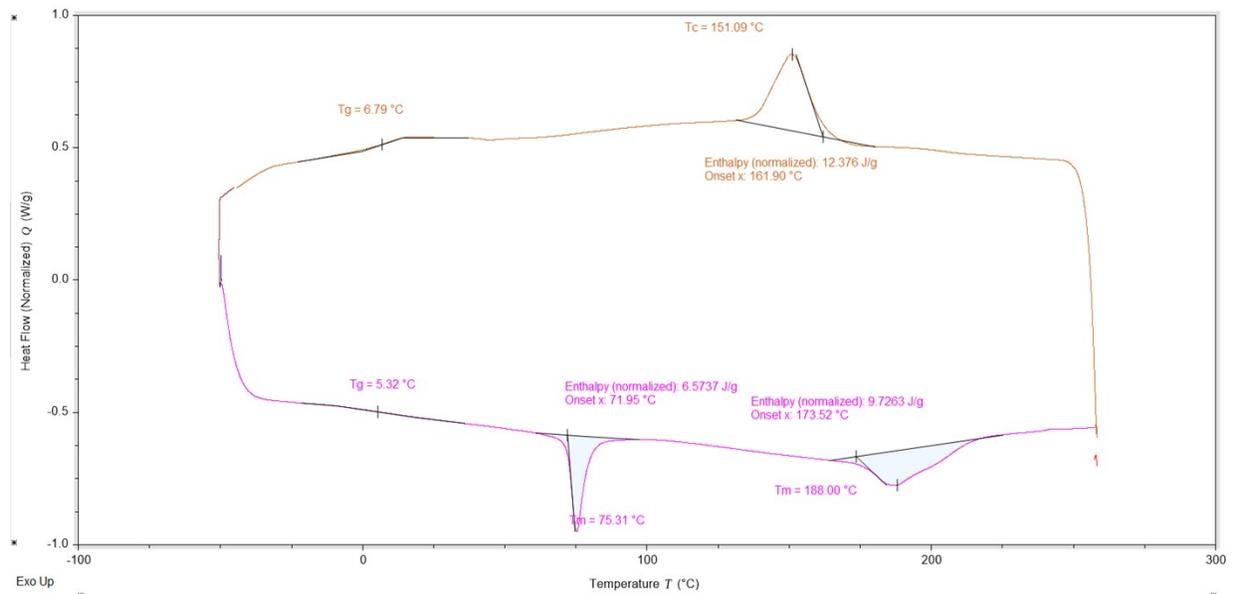


# Entry 6

## First Cycle

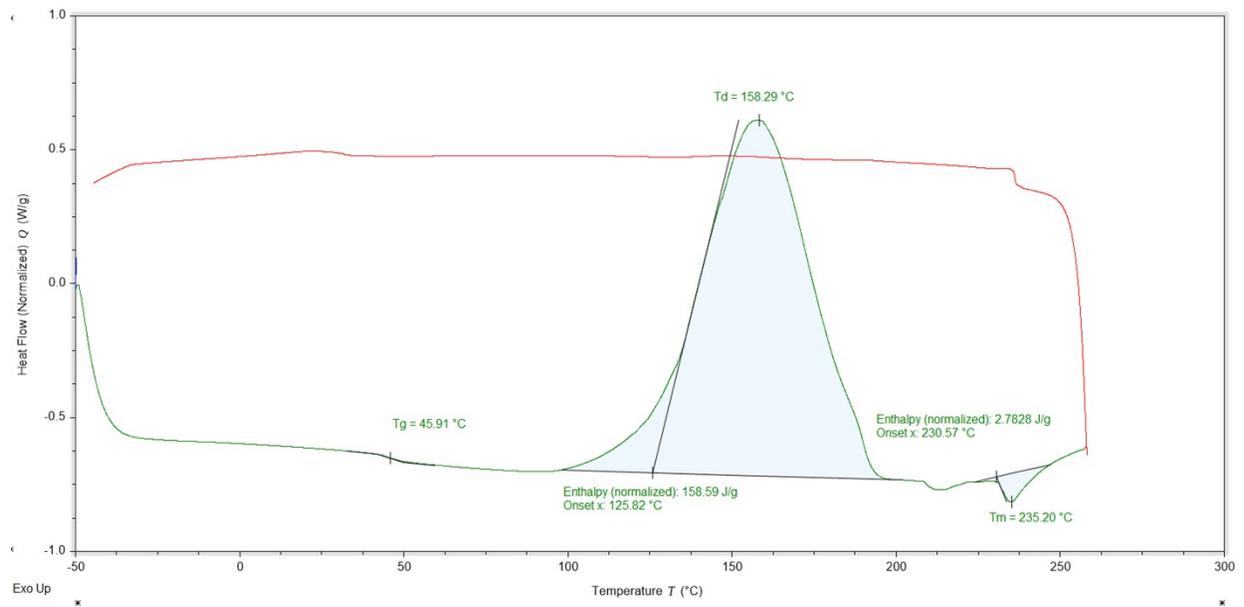


## Second Cycle



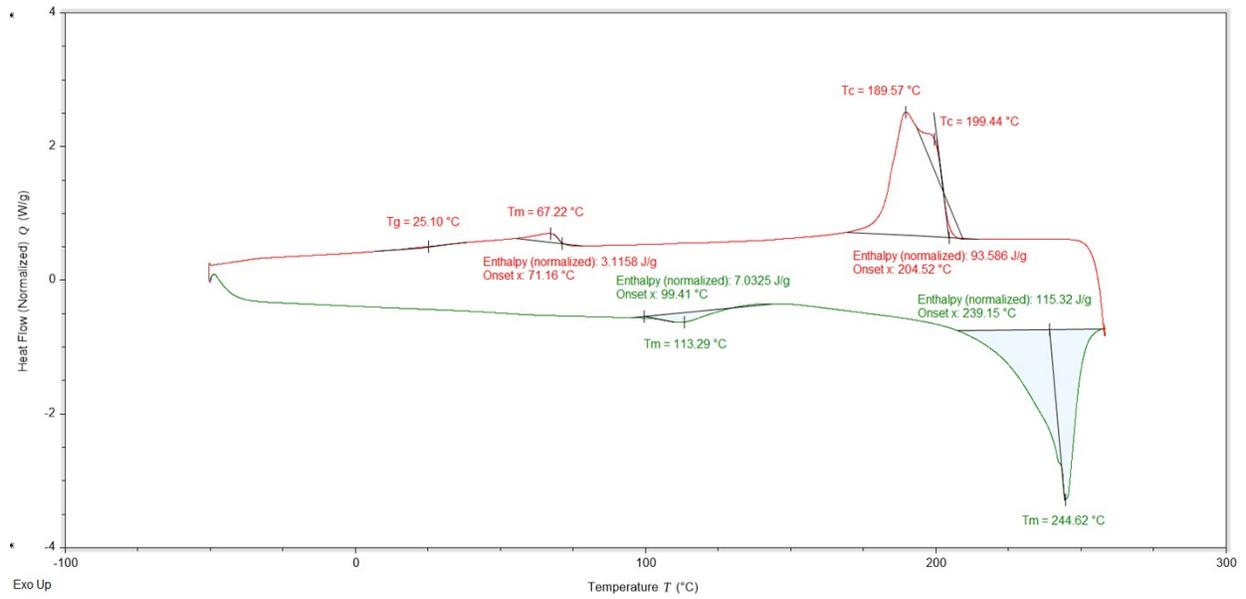
# Entry 7

## First Cycle

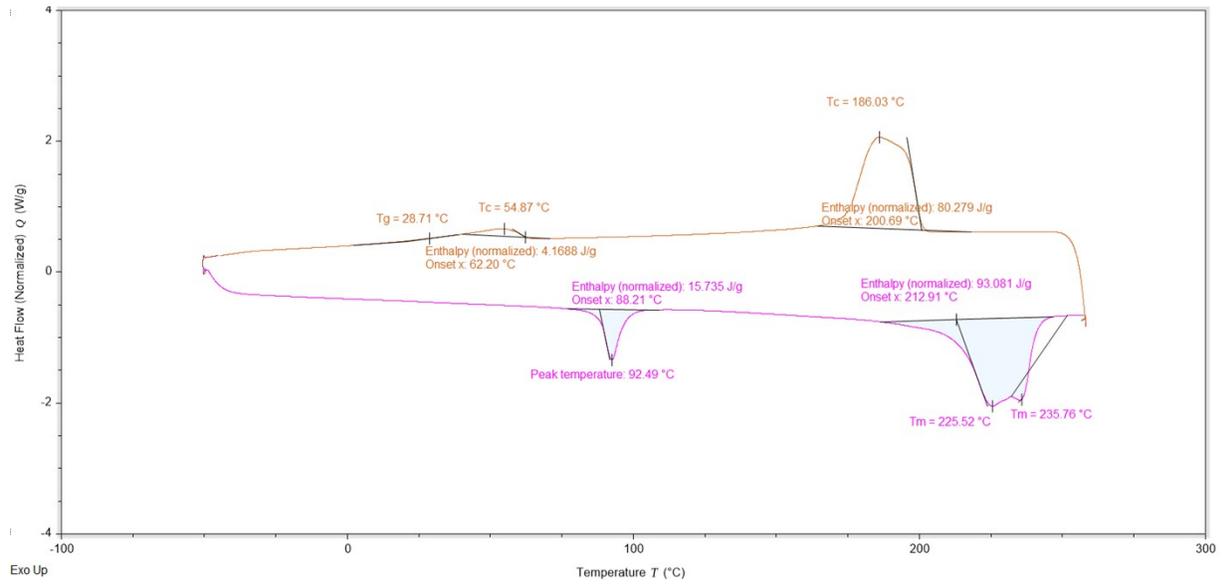


# Entry 8

## First Cycle



## Second Cycle



# Entry 9

## First Cycle

