# Supporting Information

# Viscoelastic, Mechanical, and Glasstomeric Properties of Precision Polyolefins Containing a Phenyl Branch at Every Five Carbons

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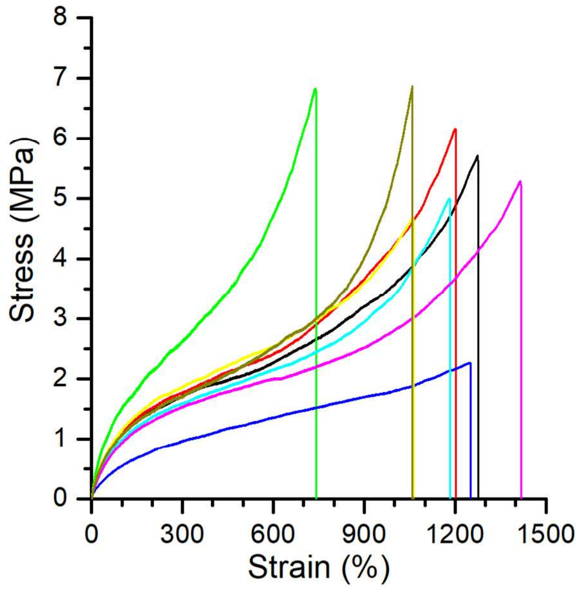


**Figure S1:** Uniaxial tensile experiments for $H_2$-P4PCP. Samples were taken at RT at a rate of 0.5 $min^{-1}$. Black curve was taken as a representative sample.

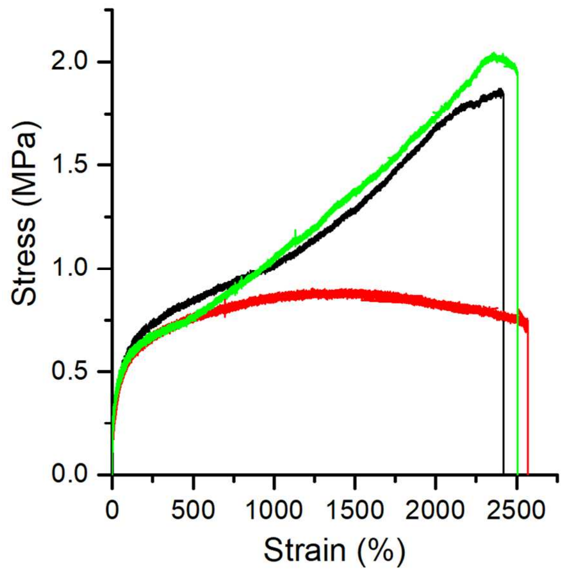


**Figure S2:** Uniaxial tensile experiments for P4PCP. Samples were taken at RT at a rate of 0.5 $min^{-1}$. Black curve was taken as a representative sample.

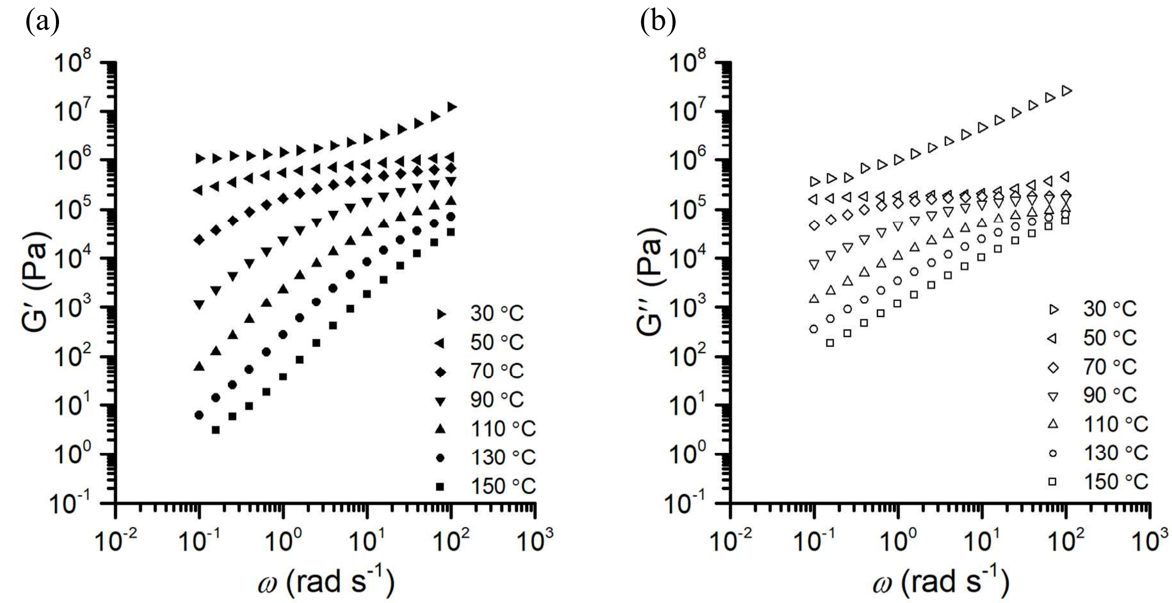


**Figure S3:** Dynamic frequency sweeps of (a) storage modulus (G′) and (b) loss modulus (G″) for $H_2$-P4PCP at varying temperatures in the linear viscoelastic regime.

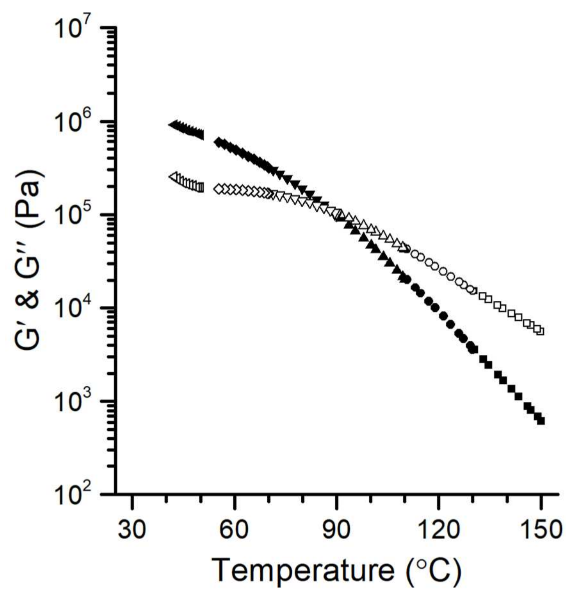


**Figure S4:** Dynamic temperature ramp of $H_2$-P4PCP monitoring storage (G′) (filled) and loss (G″) (open) moduli.

**Table S1:** Strain % and shift factors ($a_T$) used to generate TTS plot of $H_2$-P4PCP (Figure 2b)

| T (ºC) | Strain (%) | $a_T$ |
|---|---|---|
| 30 | 0.01 | 180000 |
| 50 | 0.1 | 300 |
| 70 | 0.5 | 10 |
| 90* | 0.7 | 1 |
| 110 | 1 | 0.14 |
| 130 | 1 | 0.04 |
| 150 | 2 | 0.012 |

* Reference temperature ($T_{ref}$)

(a) (b)

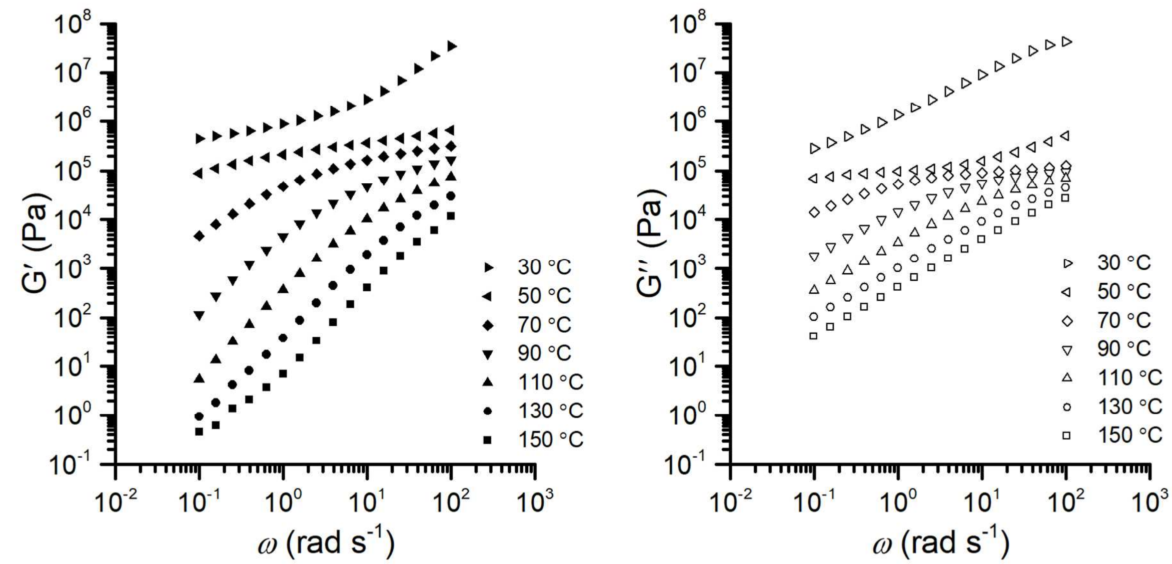


**Figure S5:** Dynamic frequency sweeps of (a) storage modulus (G′) and (b) loss modulus (G″) for P4PCP at varying temperatures in the linear viscoelastic regime.

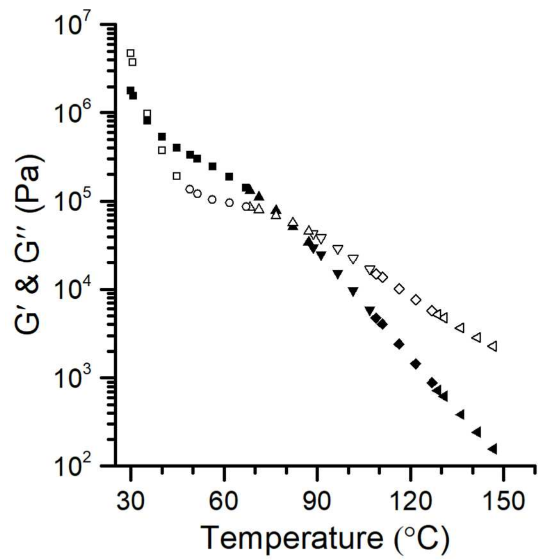


**Figure S6:** Dynamic temperature ramp of P4PCP monitoring storage (G′) (filled) and loss (G″) (open) moduli.

**Table S2:** Strain % and shift factors ($a_T$) used to generate TTS plot of P4PCP (Figure 2a)

| T (ºC) | Strain (%) | $a_T$ |
|---|---|---|
| 30 | 0.01 | 100000 |
| 50 | 0.1 | 250 |
| 70 | 0.5 | 10 |
| 90* | 0.7 | 1 |
| 110 | 1 | 0.2 |
| 130 | 1 | 0.05 |
| 150 | 2 | 0.02 |

* Reference temperature ($T_{ref}$)

Density was temperature corrected following the procedure outlined by Van Krevelen[1-3], the steps are outlined in Equations S1-S3.

**Equation S1:** Density of a polymer (ρ) at a given temperature T, where $M_o$ = molecular weight of the repeat unit and V(T) is the molar volume occupied at a given temperature

$$\rho(T) = \frac{M_o}{V(T)}$$

**Equation S2:** Calculation of the van der Waals volume ($V_W$)

$$V_W = \frac{V(297\ K)}{1.6}$$

**Equation S3:** Molar volume at a given temperature T, where T = $T_{ref}$ (297 K)

$$V(T) = V(297\ K) + 1.0 * 10^{-3}(T - 297)V_W$$

**Table S3:** Values used for calculating ρ (90 °C) for P4PCP and $H_2$-P4PCP used in equations S1-S3.

| Sample | ρ (24 °C) (g mL $^{-1}$) | $M_o$ (g mol$^{-1}$) | V (297 K) (cm$^3$ mol$^{-1}$) | $V_W$ (cm$^3$ mol$^{-1}$) | ρ (363 K) (g mL $^{-1}$) |
|---|---|---|---|---|---|
| P4PCP | 1.04 | 144.22 | 138.67 | 86.67 | 0.999 |
| $H_2$-P4PCP | 1.02 | 146.11 | 143.24 | 89.53 | 0.980 |

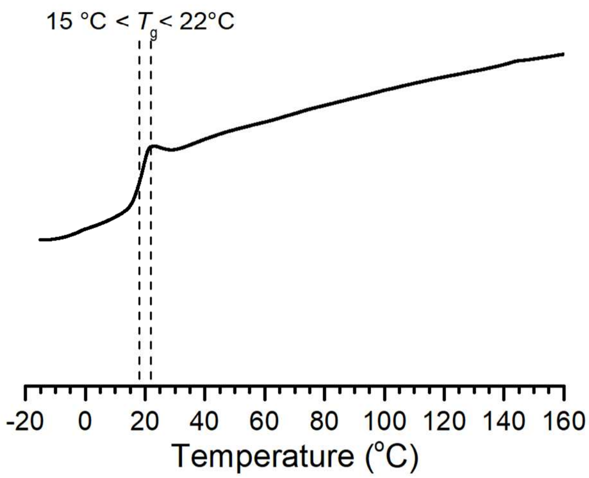


**Figure S7:** DSC thermogram (endo up) of $H_2$-P4PCP. Temperature was swept from -30 to 180 °C at a rate of 10 °C min$^{-1}$

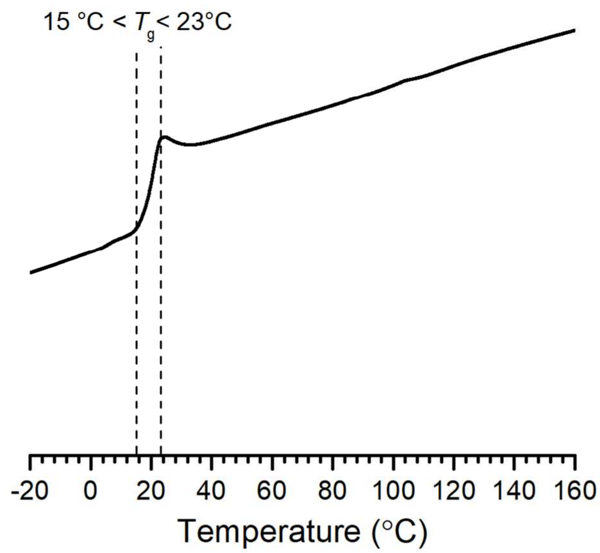


**Figure S8:** DSC thermogram (endo up) of P4PCP. Temperature was swept from -30 to 180 °C at a rate of 10 °C min$^{-1}$

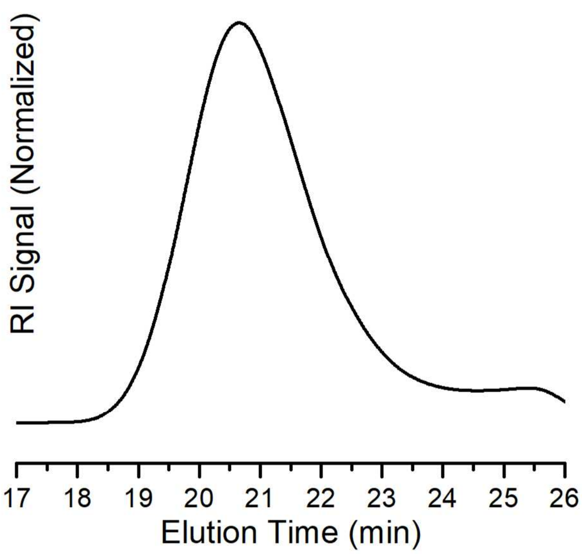


**Figure S9:** Differential refractive index (RI) signal from SEC analysis of $H_2$-P4PCP sample.

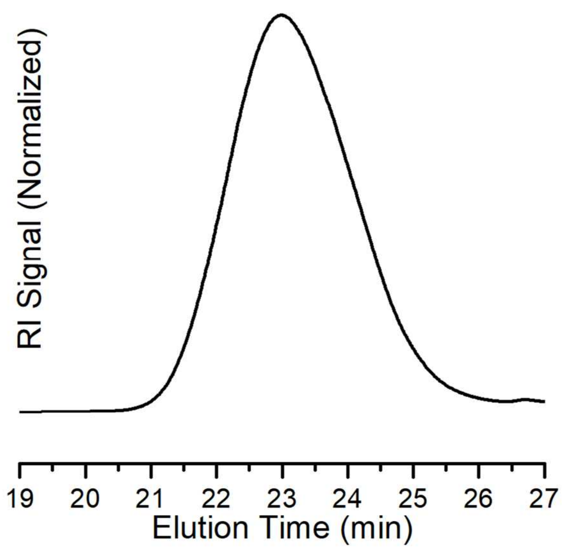


**Figure S10:** Differential refractive index (RI) signal from SEC analysis of P4PCP sample.

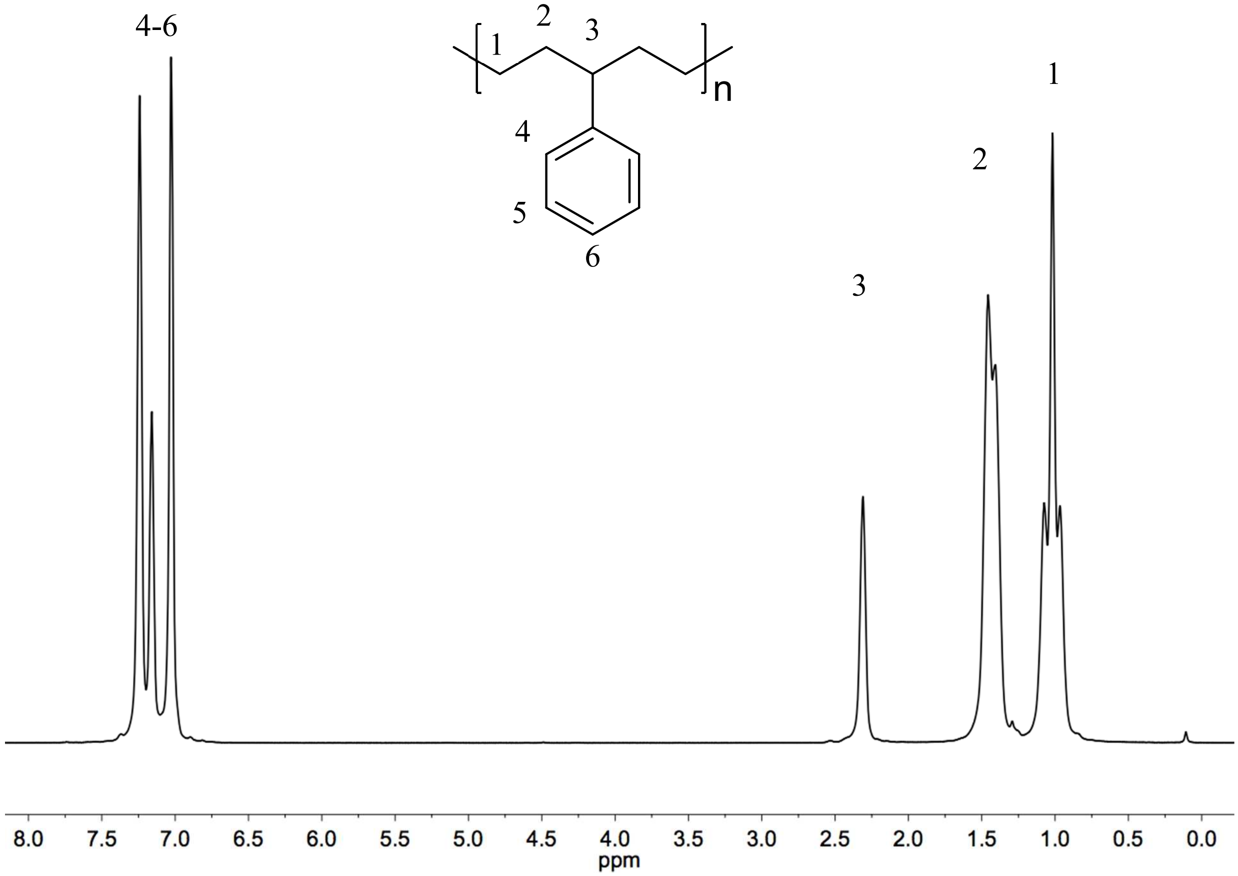


**Figure S11:** $^{1}$H-NMR spectra of $H_2$-P4PCP (600 MHz, chloroform-*d*)

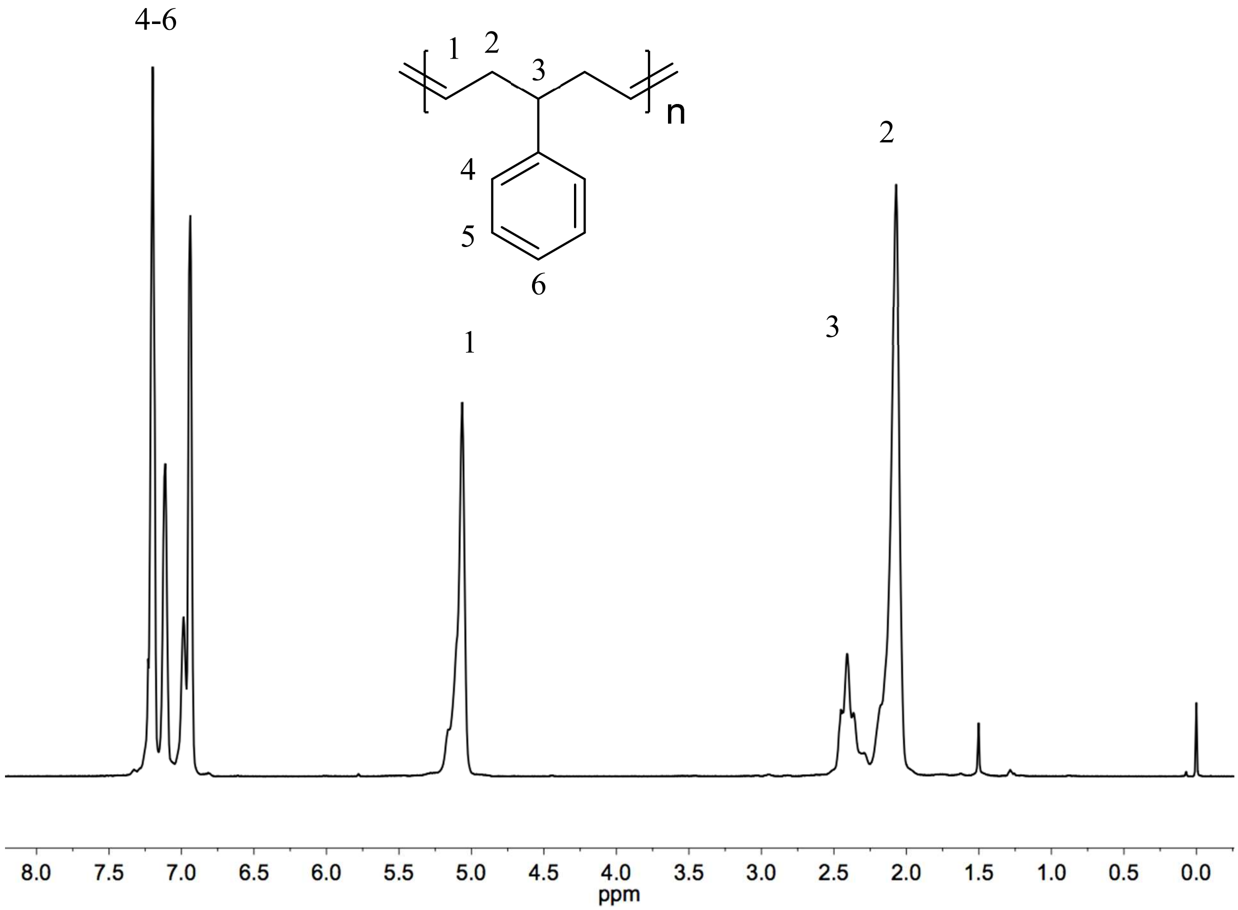


**Figure S12:** $^{1}$H-NMR spectra of P4PCP (600 MHz, chloroform-*d*)

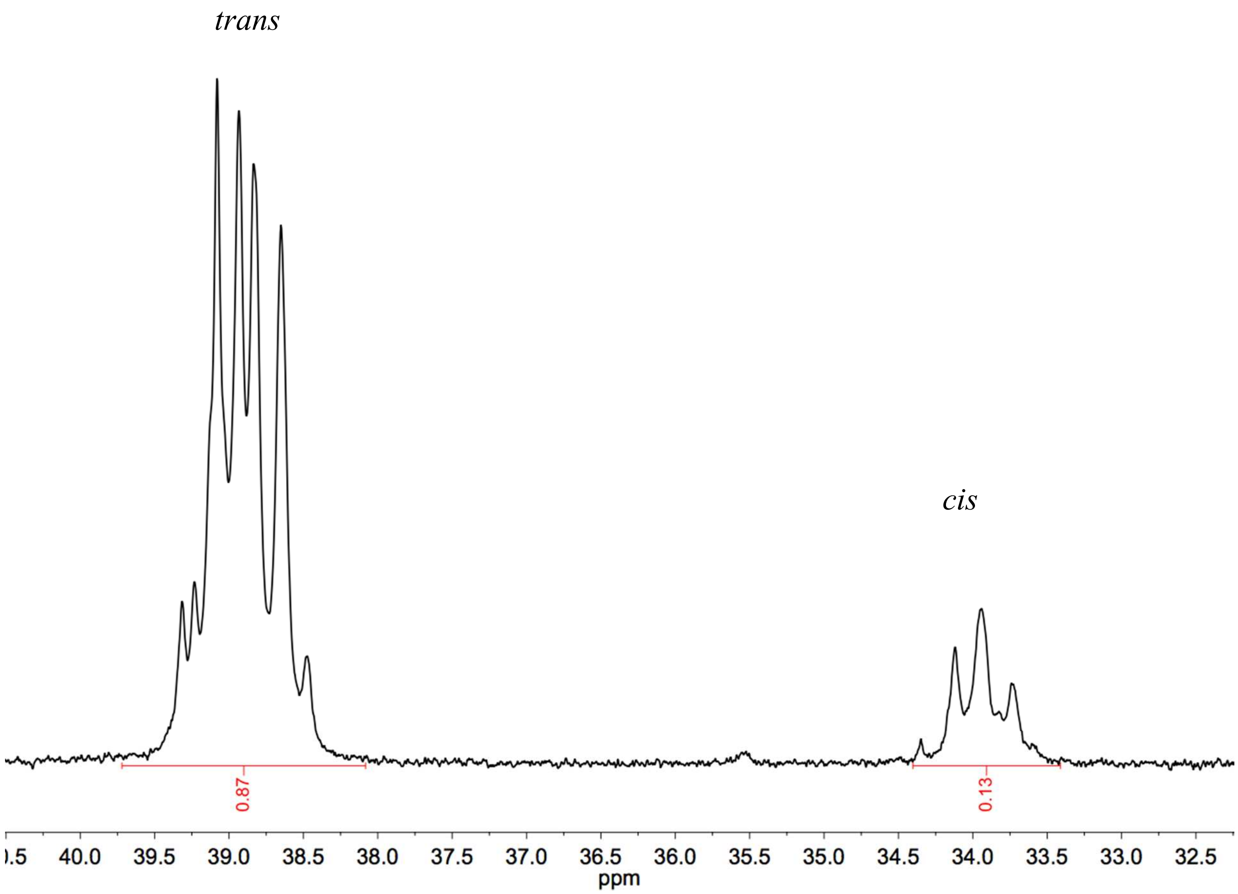


**Figure S13:** Inverse gated decoupling $^{13}$C-NMR spectra of P4PCP (151 MHz, chloroform-*d*)


**Figure S14:** Pictures of $H_2$-P4PCP recovering its original shape (right) after being coiled around tweezers and cooled to 0 °C for 1 min (left). Full recovery occurred at RT over 2 min and 45 sec.

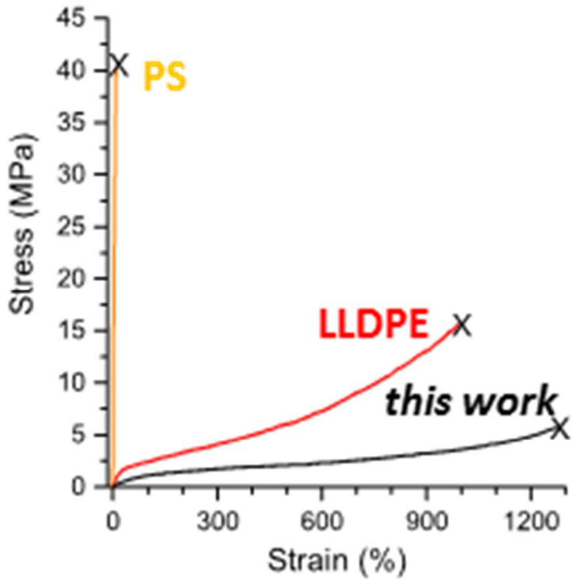


**Figure S15.** The plot comparison shown in the TOC graphic for this manuscript contains mechanical testing comparison between polystyrene (PS) obtained from Sigma-Aldrich ($M_n$ = 170.0 kDa, $Đ$ = 2.06) and linear low density polyethylene (LLDPE) obtained from DOW Chemical Company as a copolymer with 6.3% octene ($M_n$ = 142.8 kDa, $Đ$ = 2.14). All uniaxial stress-strain experiments were performed using at a constant 0.5 min$^{-1}$ strain rate.

**References**

1. Van Krevelen, D. W.; Te Nijenhuis, K., *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*. Elsevier: 2009; p 1030.
2. Ganewatta, M. S.; Ding, W.; Rahman, M. A.; Yuan, L.; Wang, Z.; Hamidi, N.; Robertson, M. L.; Tang, C., Biobased Plastics and Elastomers from Renewable Rosin via "Living" Ring-Opening Metathesis Polymerization. *Macromolecules* **2016,** *49* (19), 7155-7164.
3. Kieber, R. J.; Silver, S. A.; Kennemur, J. G., Stereochemical effects on the mechanical and viscoelastic properties of renewable polyurethanes derived from isohexides and hydroxymethylfurfural. *Polym. Chem* **2017,** *8* (33), 4822-4829.