

Supporting Information

Stereochemical Effects on the Mechanical and Viscoelastic Properties of Renewable Polyurethanes Derived from Isohexides and Hydroxymethylfurfural

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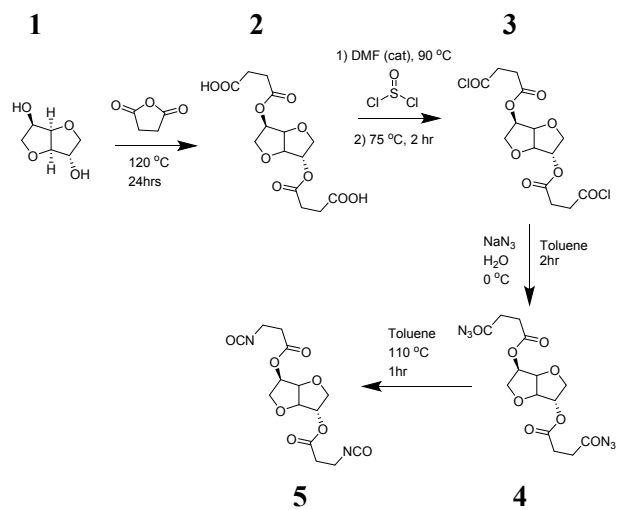
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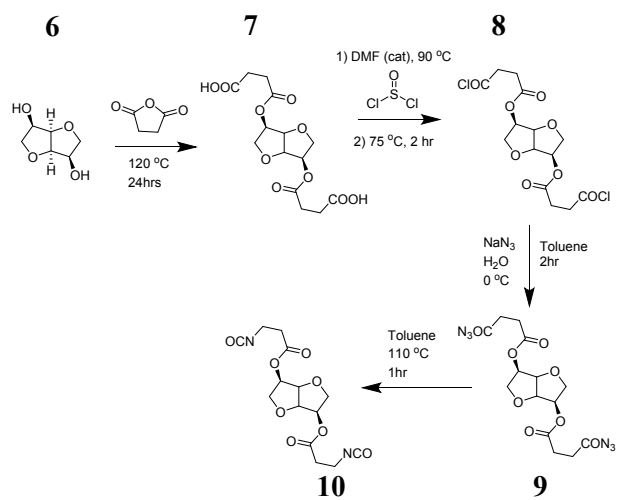
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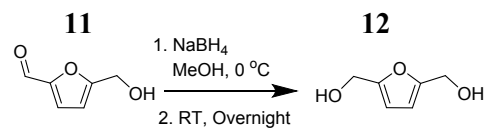
Scheme S1: Synthesis of ISBIP.



Scheme S2: Synthesis IMBIP.



Scheme S3: Synthesis of BHMFB



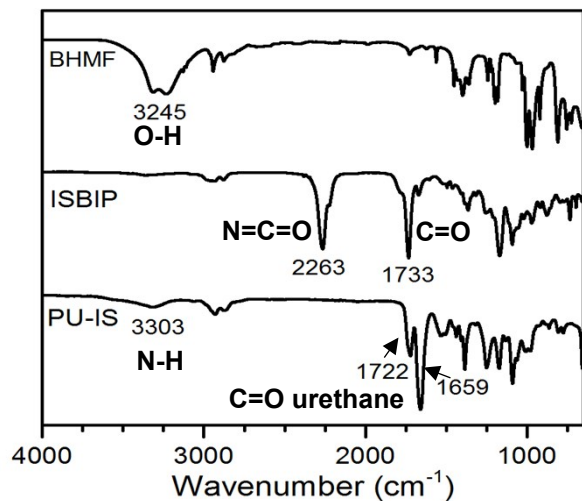


Figure S1: ATR-FTIR of BHMf, ISBIP, and an example polyurethane (PU-IS)

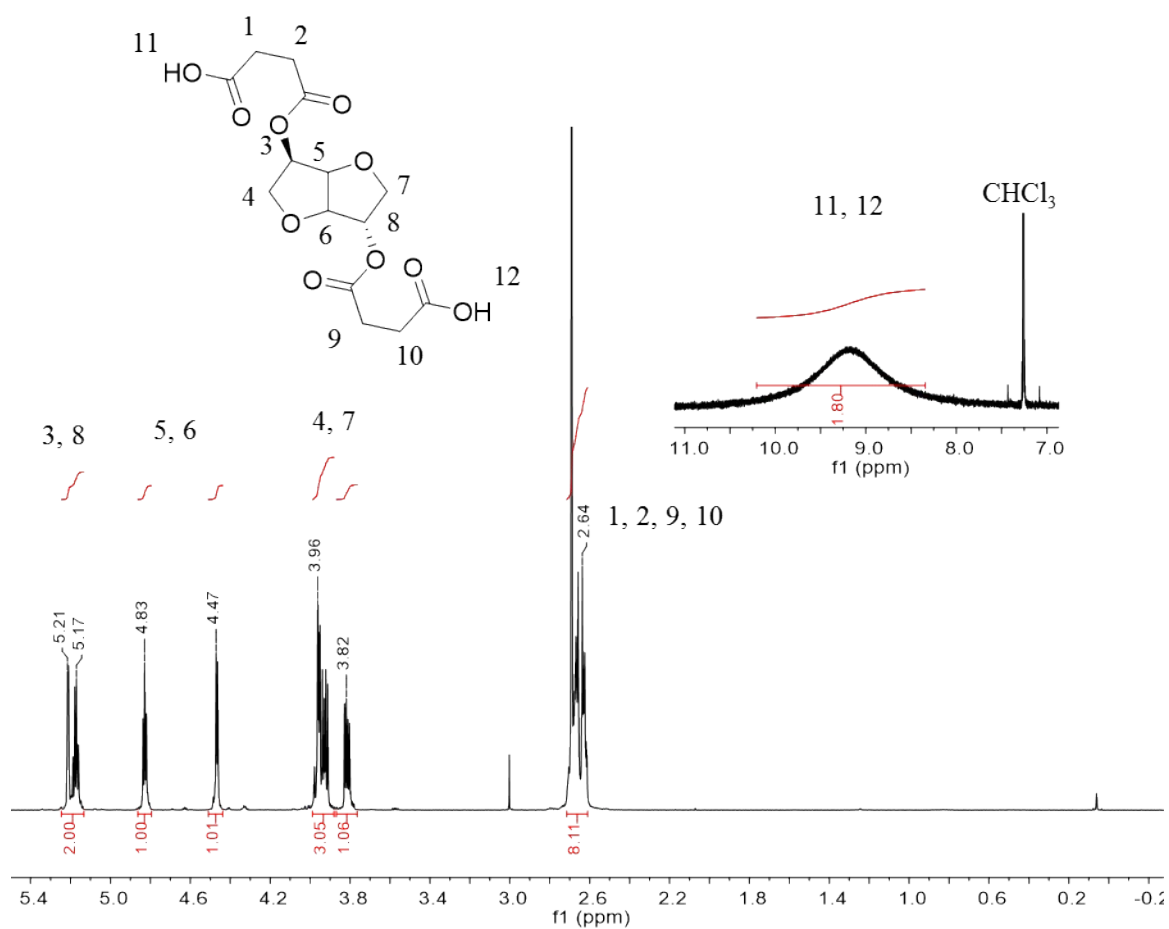


Figure S2: ^1H NMR of Isosorbide Extended Carboxylic Acid (**2**). Inset shows COOH peak (600 MHz, Chloroform-*d*)

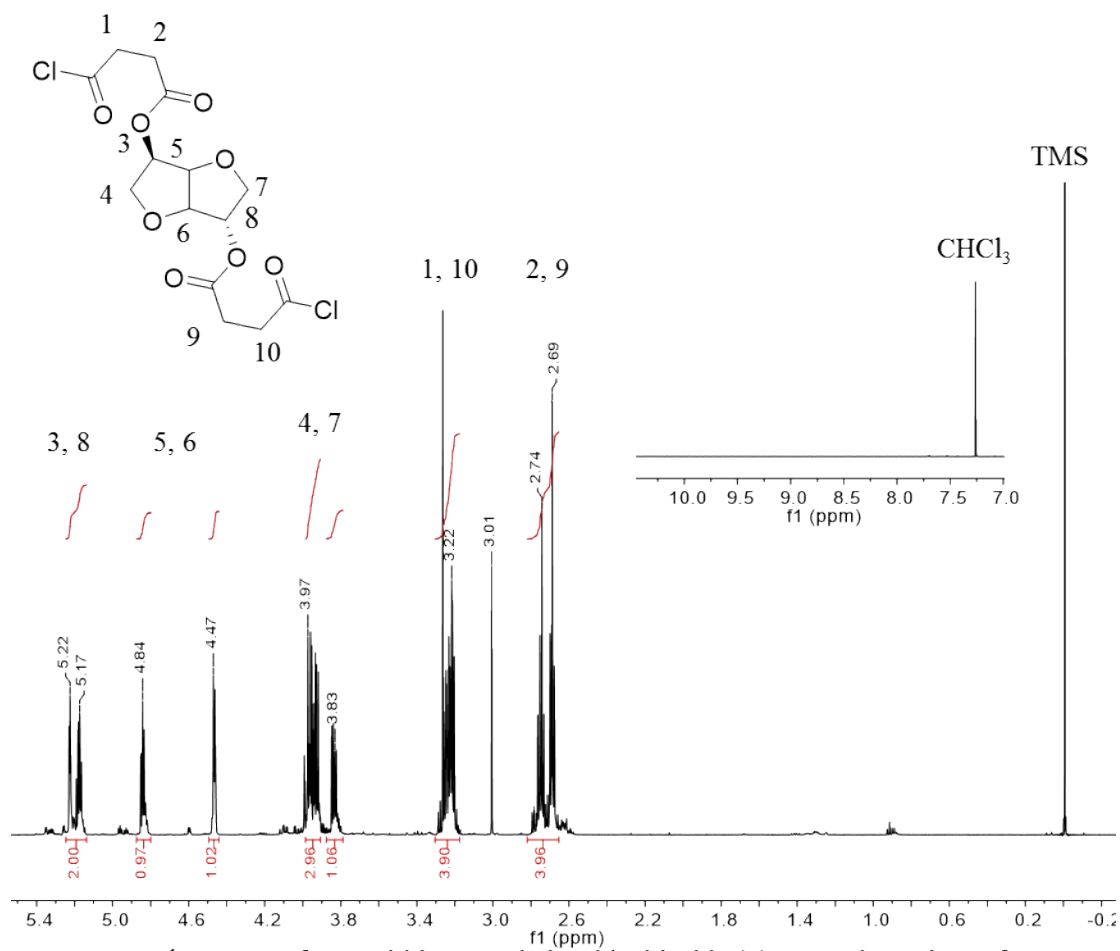


Figure S3: ¹H NMR of Isosorbide Extended Acid Chloride (**3**). Inset shows loss of COOH peak (600 MHz, Chloroform-*d*)

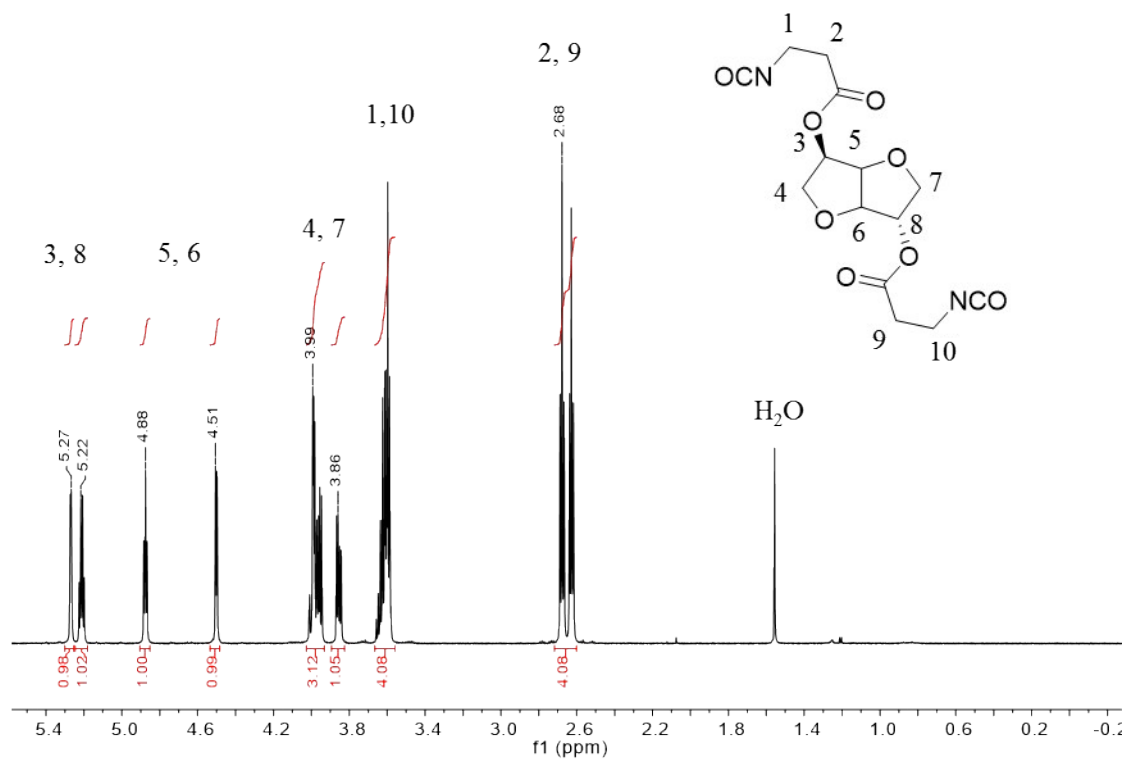


Figure S4: ¹H NMR of ISBIP (5) (600 MHz, Chloroform-*d*)

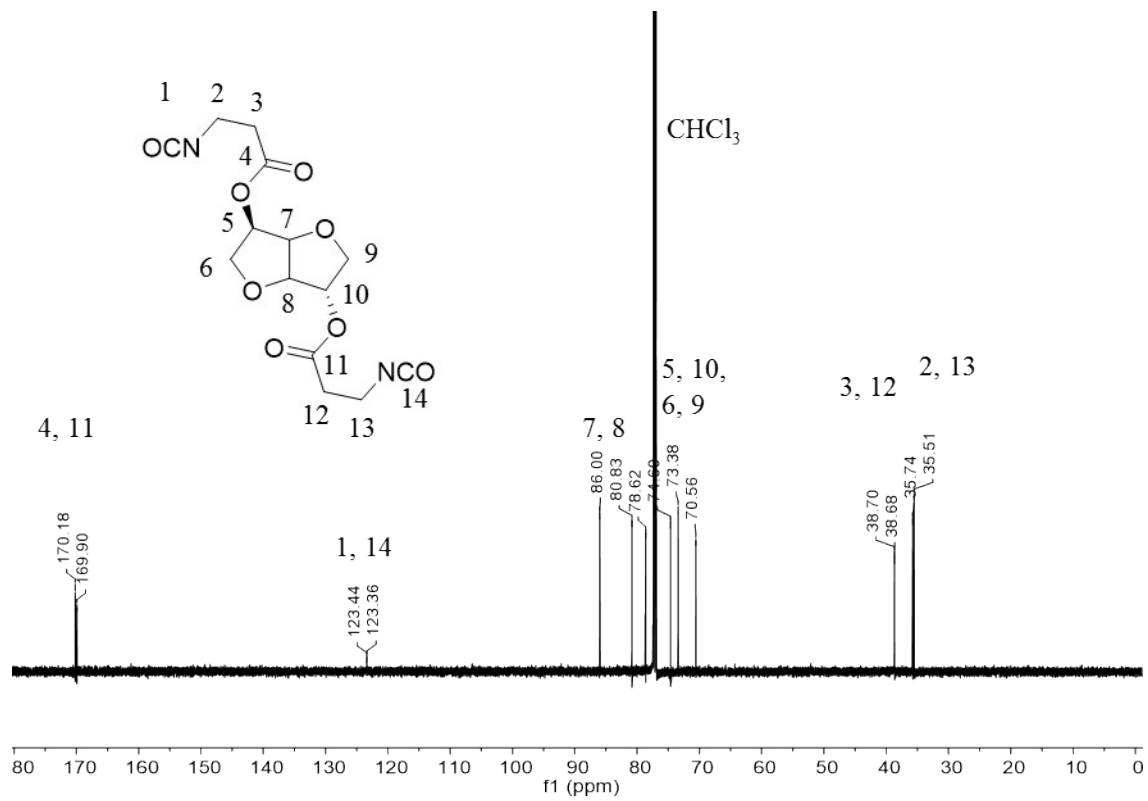


Figure S5: ¹³C NMR of ISBIP (5) (151 MHz, Chloroform-*d*)

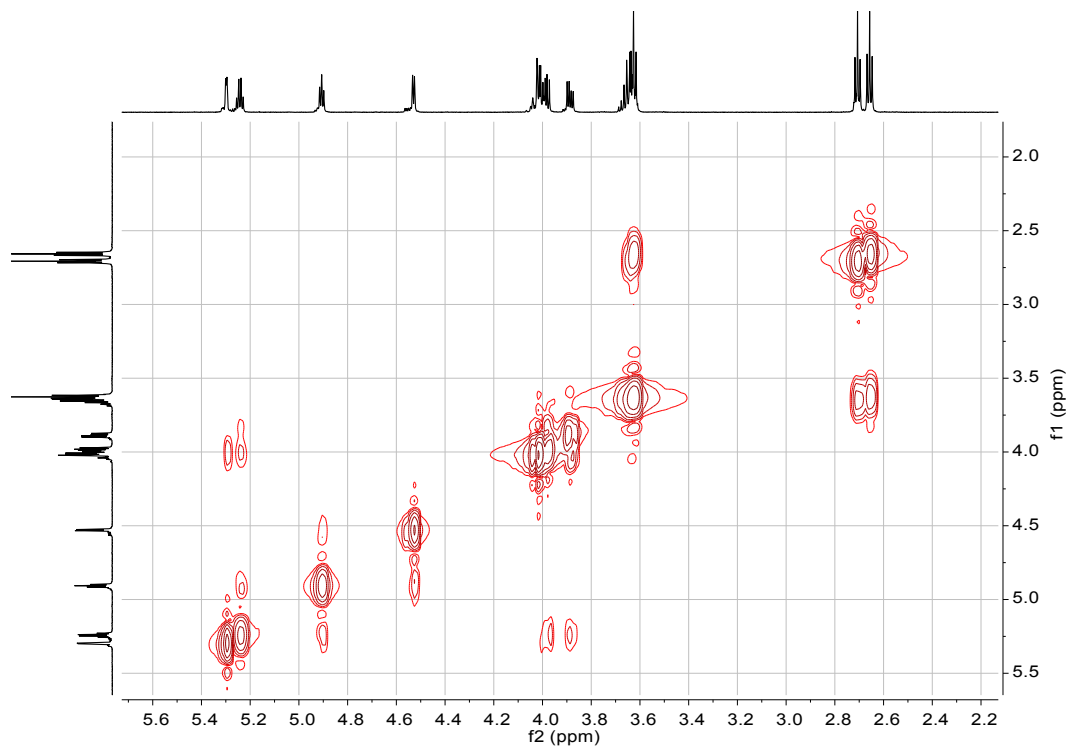


Figure S6: COSY ISBIP(5) (600 MHz, 25 °C, chloroform-*d*)

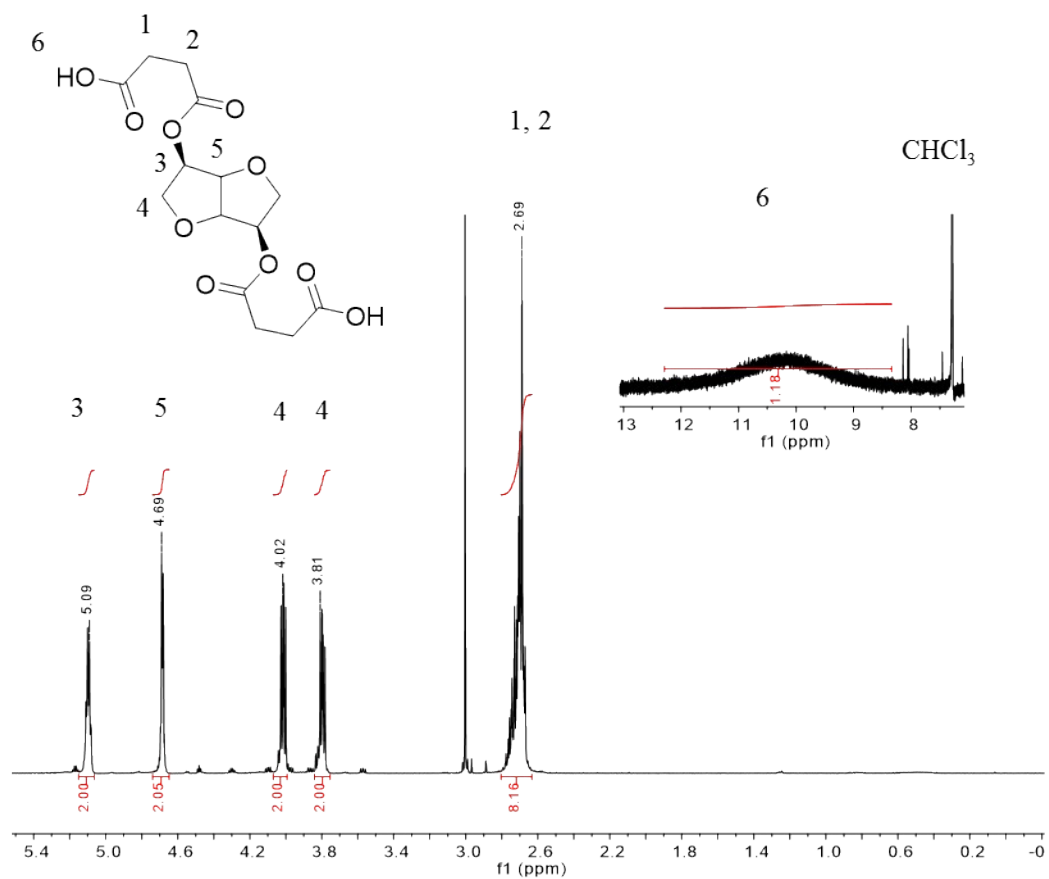


Figure S7: ¹H NMR of Isomannide Extended Carboxylic Acid (7). Inset shows COOH peak (600 MHz, Chloroform-*d*)

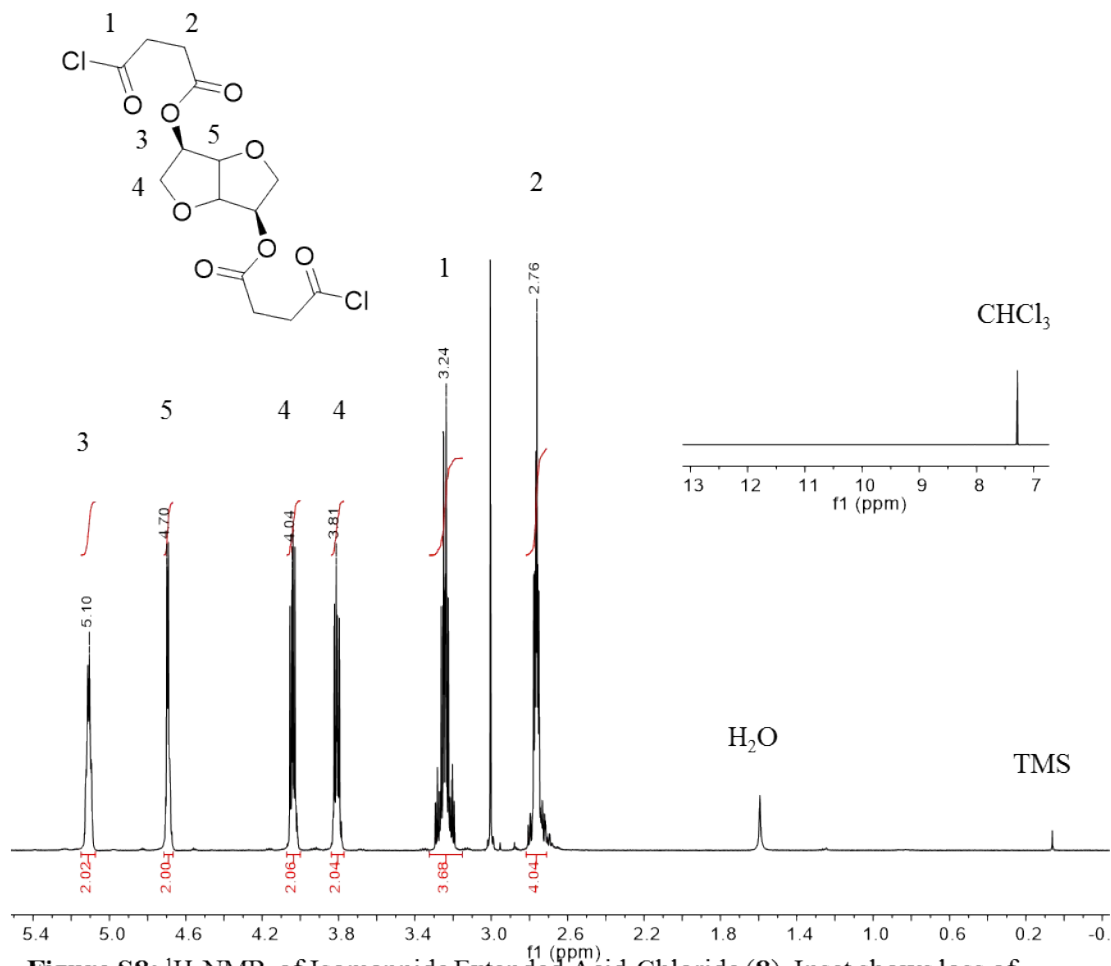


Figure S8: ¹H NMR of Isomannide Extended Acid Chloride (**8**). Inset shows loss of COOH peak (600 MHz, Chloroform-*d*)

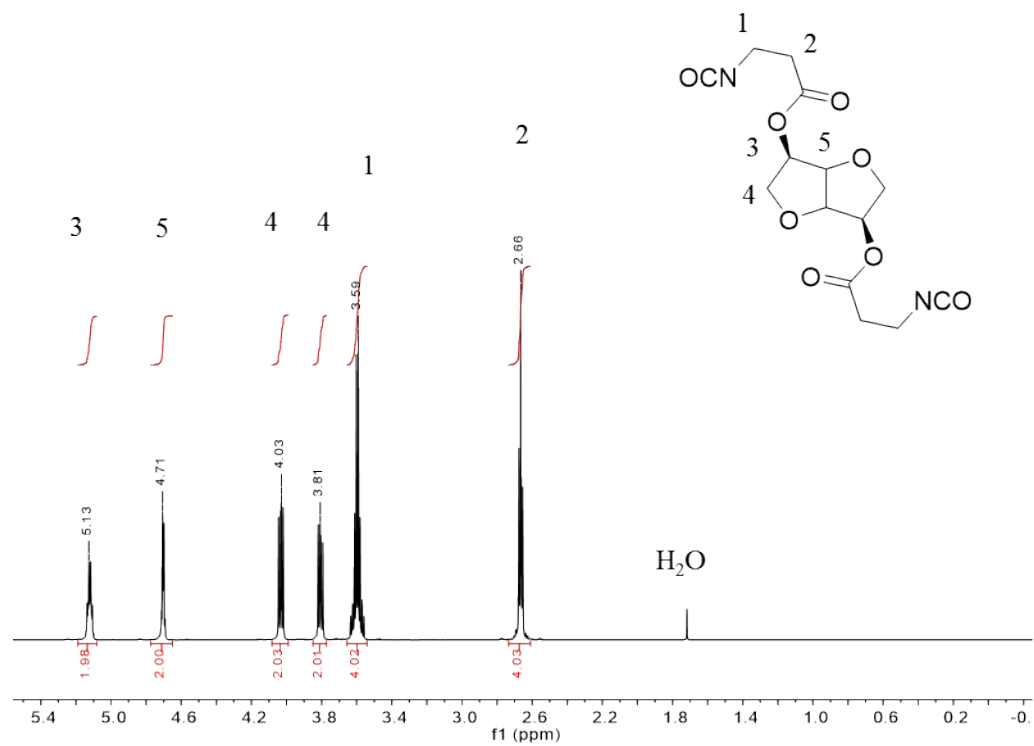


Figure S9: ¹H NMR of IMBIP (**10**) (600 MHz, Chloroform-*d*)

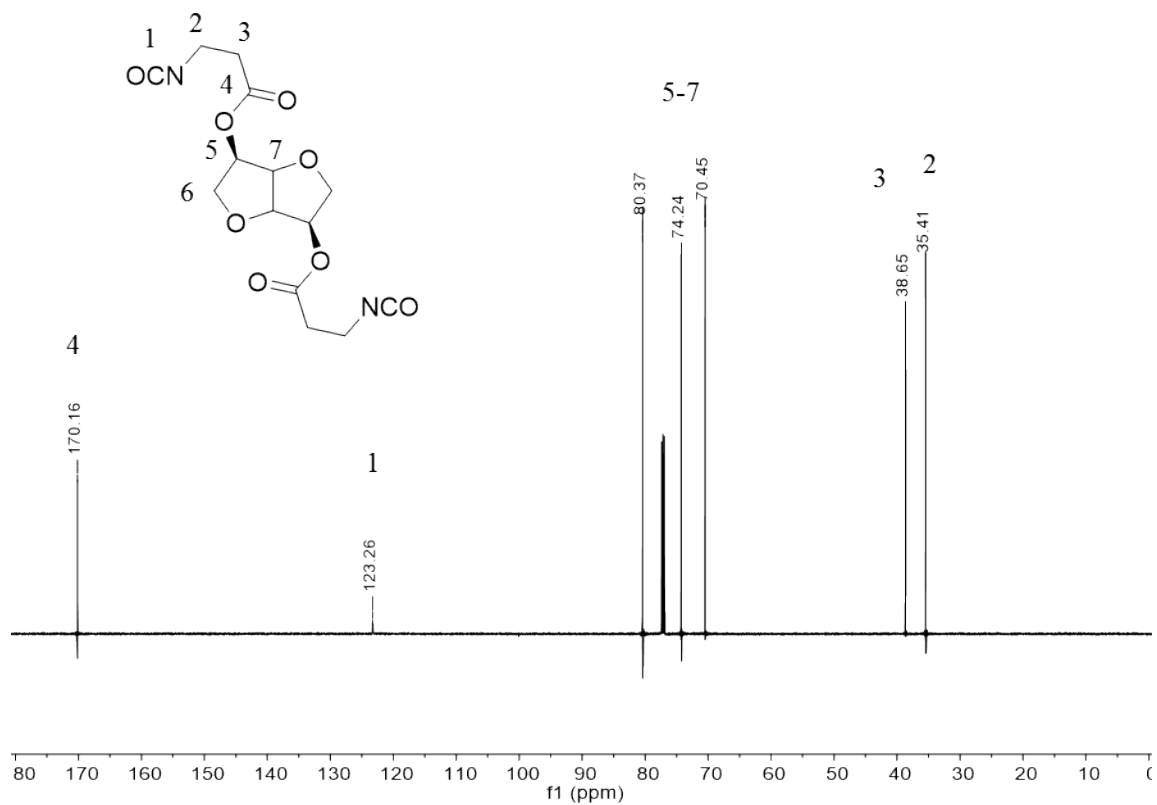


Figure S10: ¹³C NMR of IMBIP (**10**) (151 MHz, Chloroform-*d*)

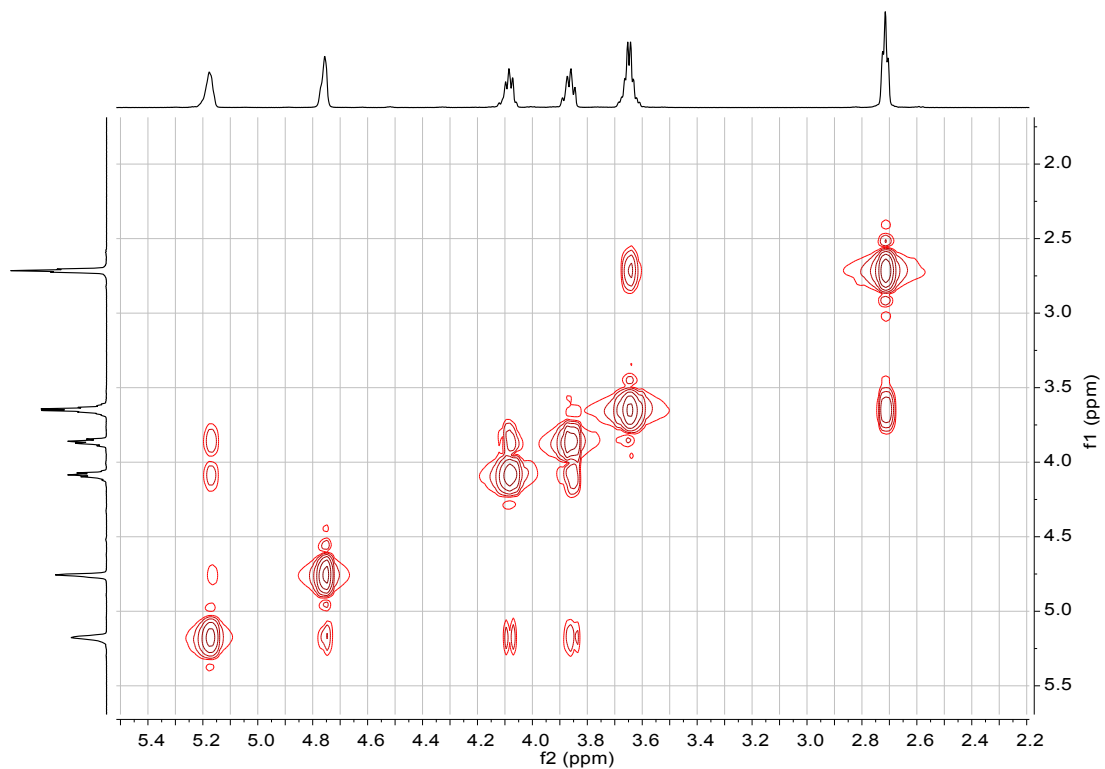


Figure S11: COSY IMBIP (**10**) (600 MHz, 25 °C, chloroform-*d*)

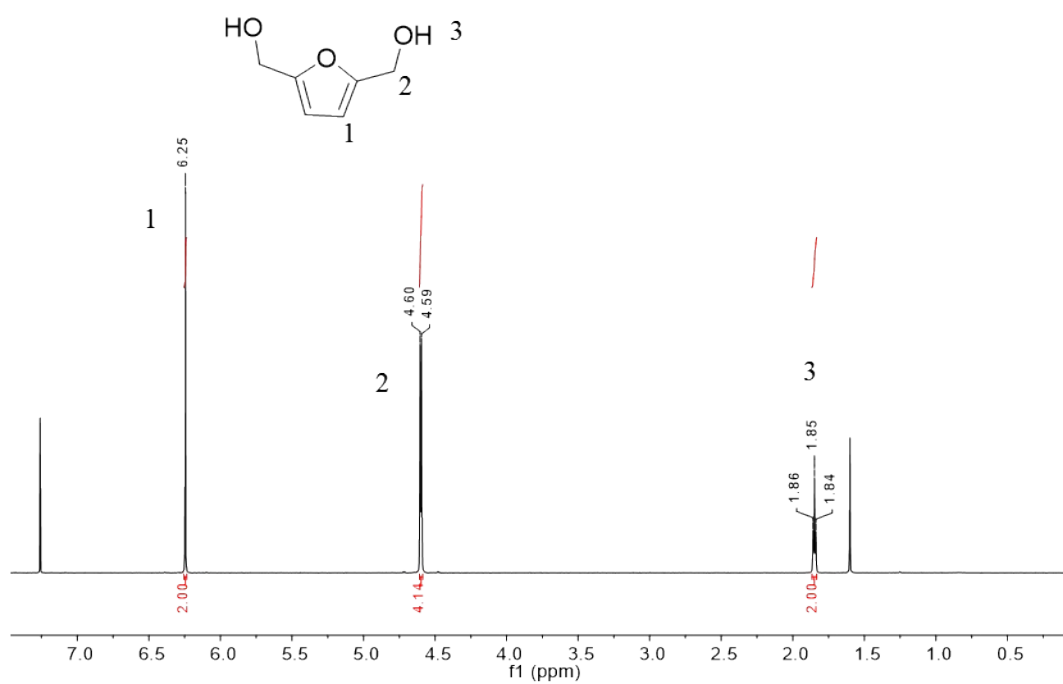


Figure S12: ¹H NMR of BHMF (12) (600 MHz, Chloroform-*d*)

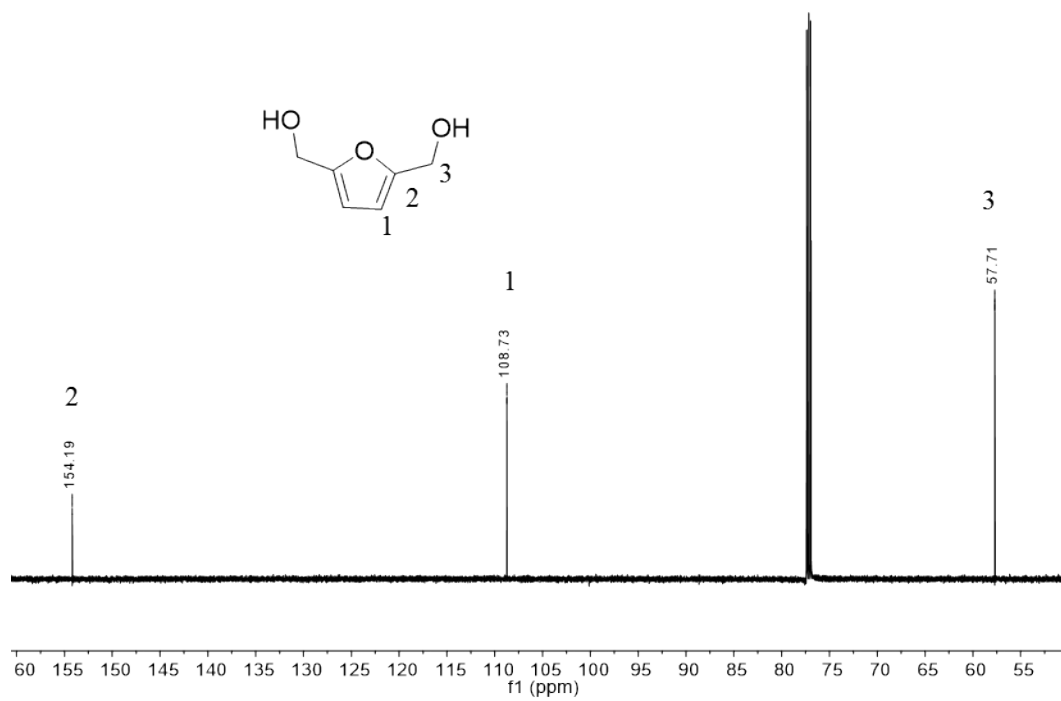


Figure S13: ^{13}C NMR of BHMF (12) (151 MHz, Chloroform-*d*)

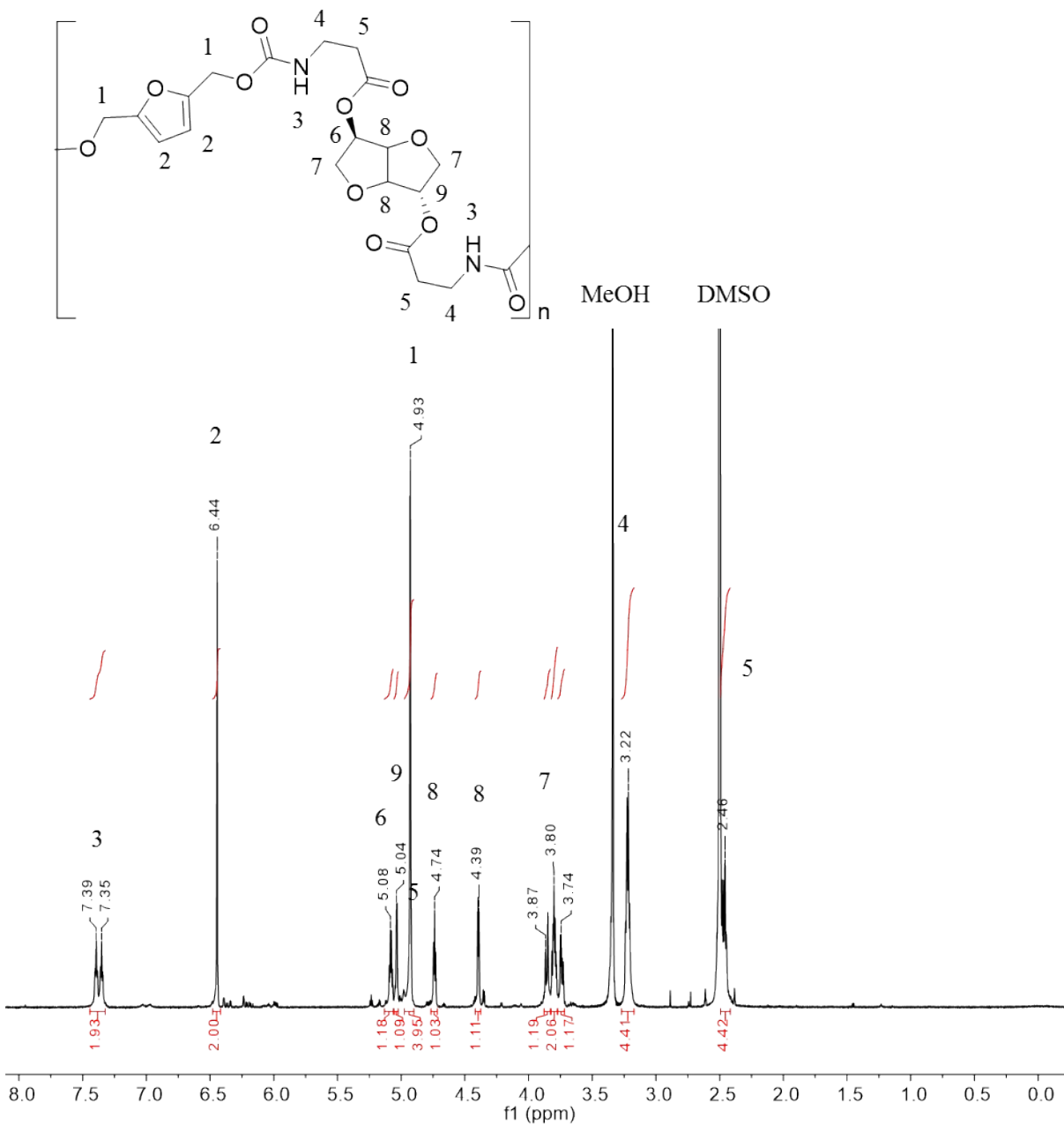


Figure S14: ^1H NMR of PU-IS (600 MHz, $\text{DMSO-}d_6$)

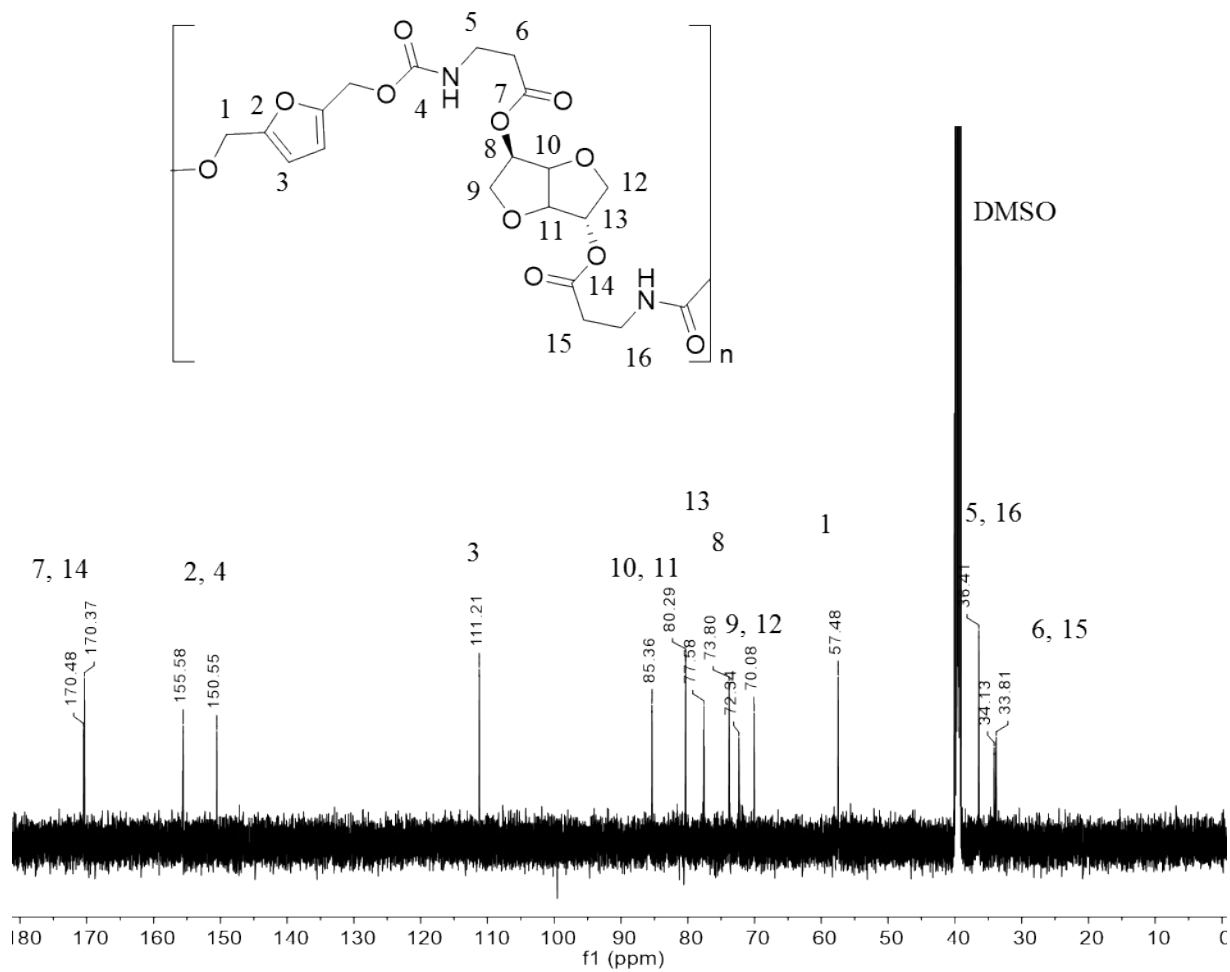


Figure S15: ^{13}C NMR of PU-IS (600 MHz, $\text{DMSO-}d_6$)

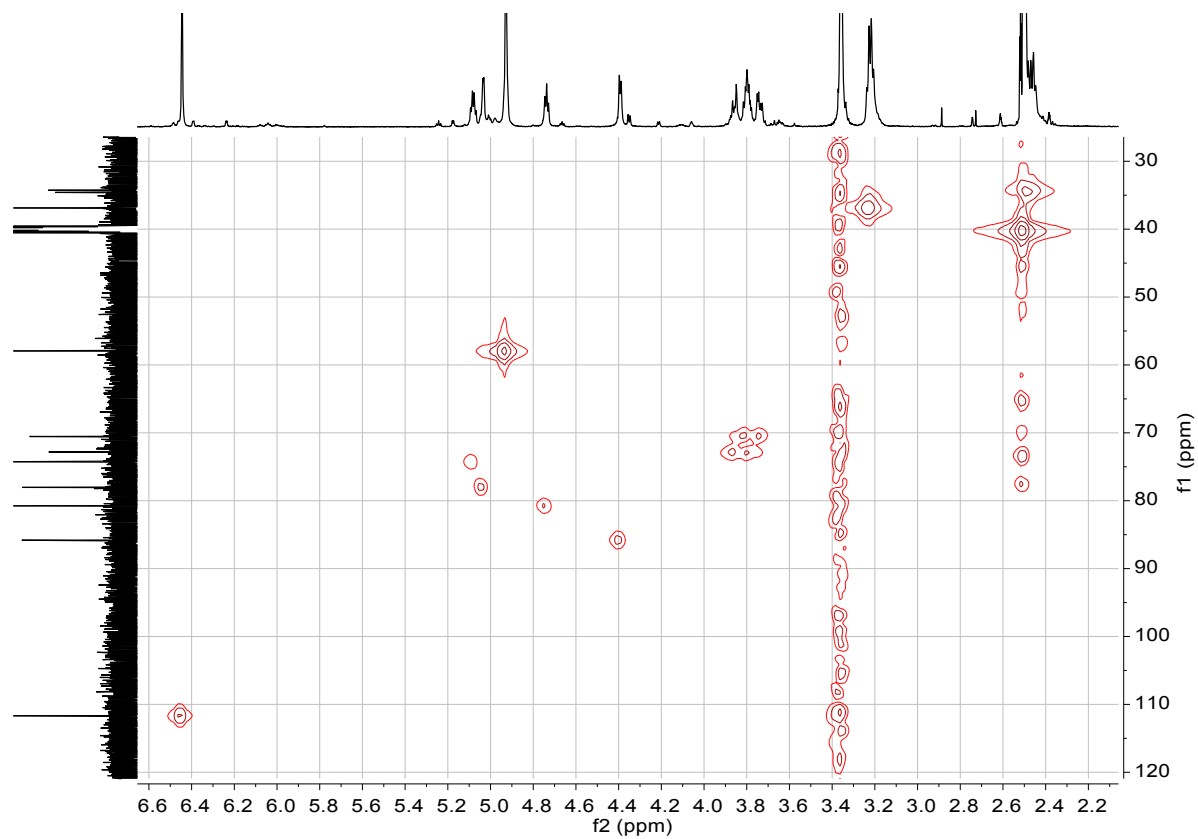


Figure S16: HMQC of PU-IS (600 MHz, 150 MHz, 25 °C, DMSO-*d*₆)

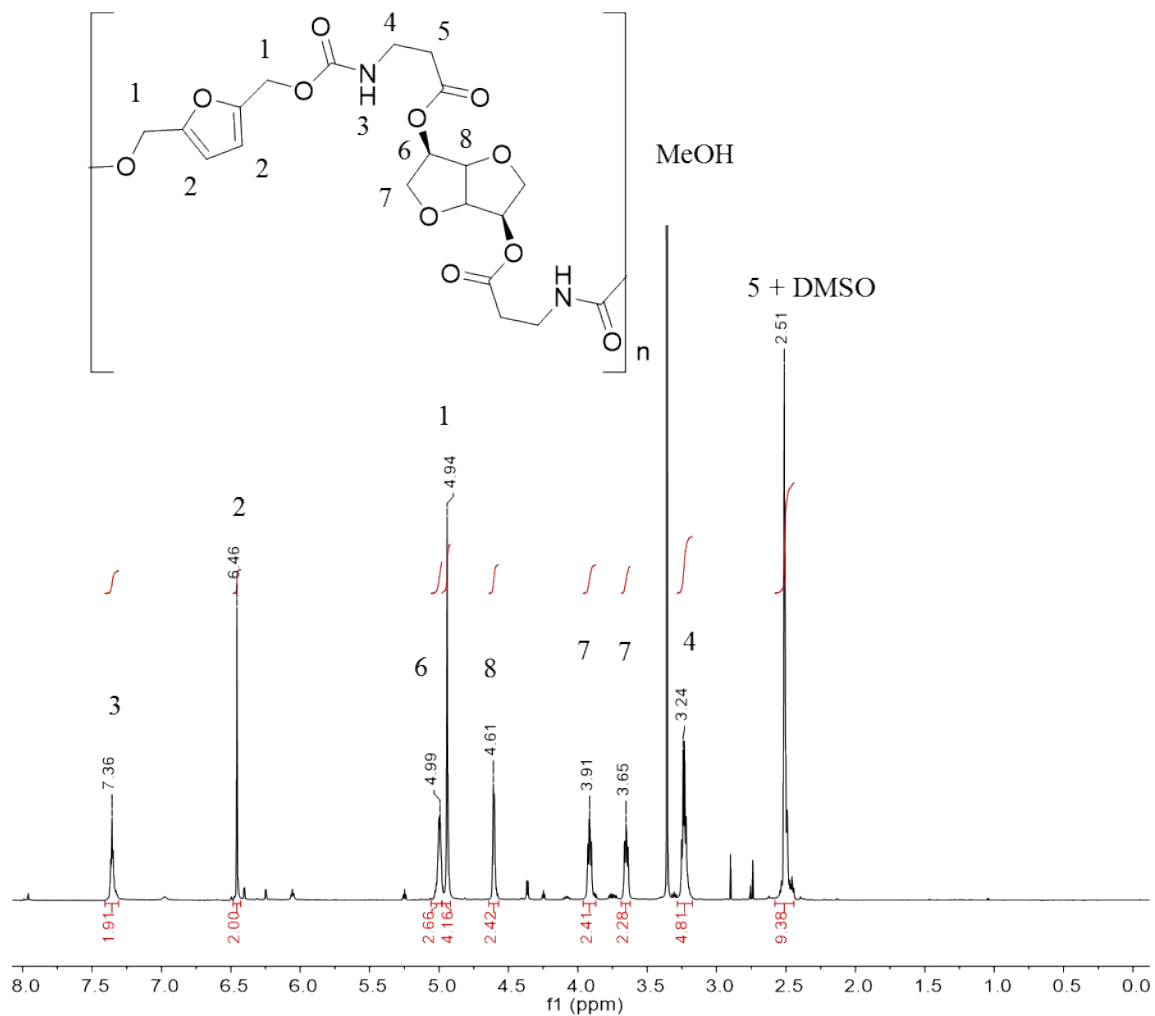


Figure S17: ¹H NMR of PU-IM (600 MHz, DMSO-*d*₆)

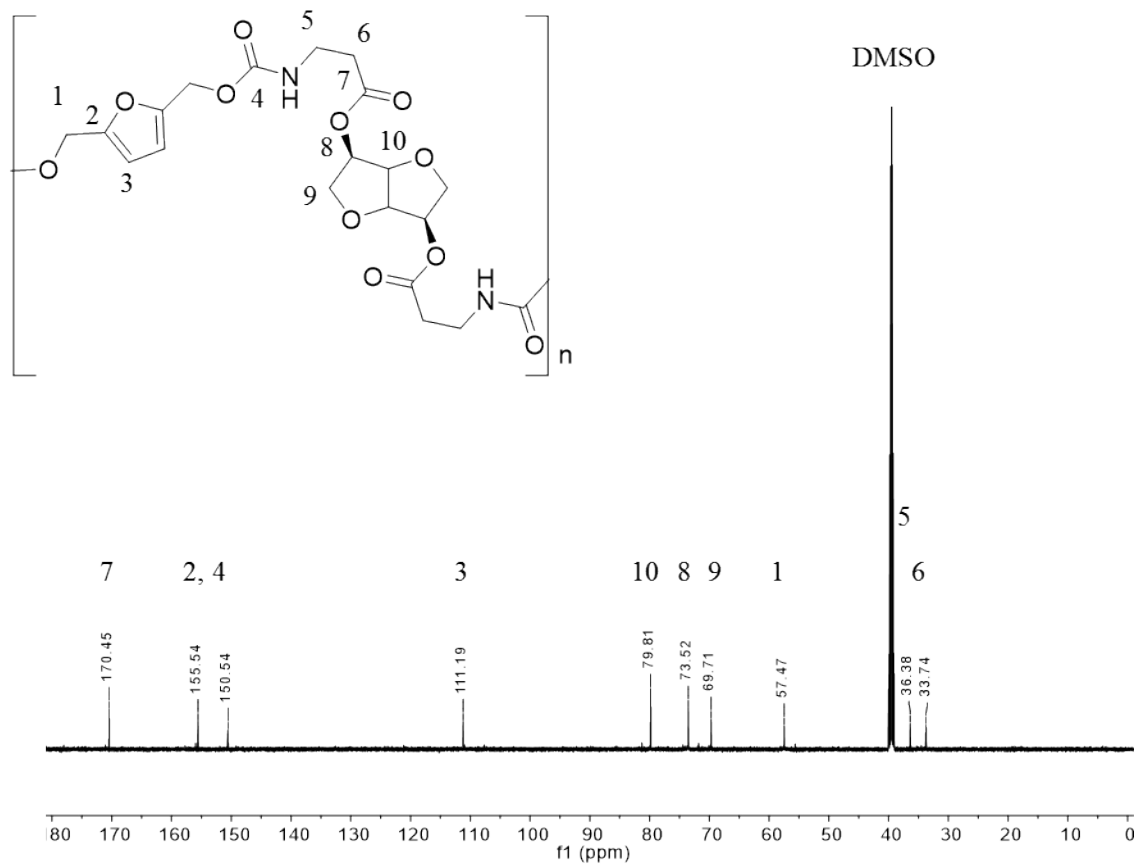


Figure S18: ^{13}C NMR of PU-IM (151 MHz, $\text{DMSO-}d_6$)

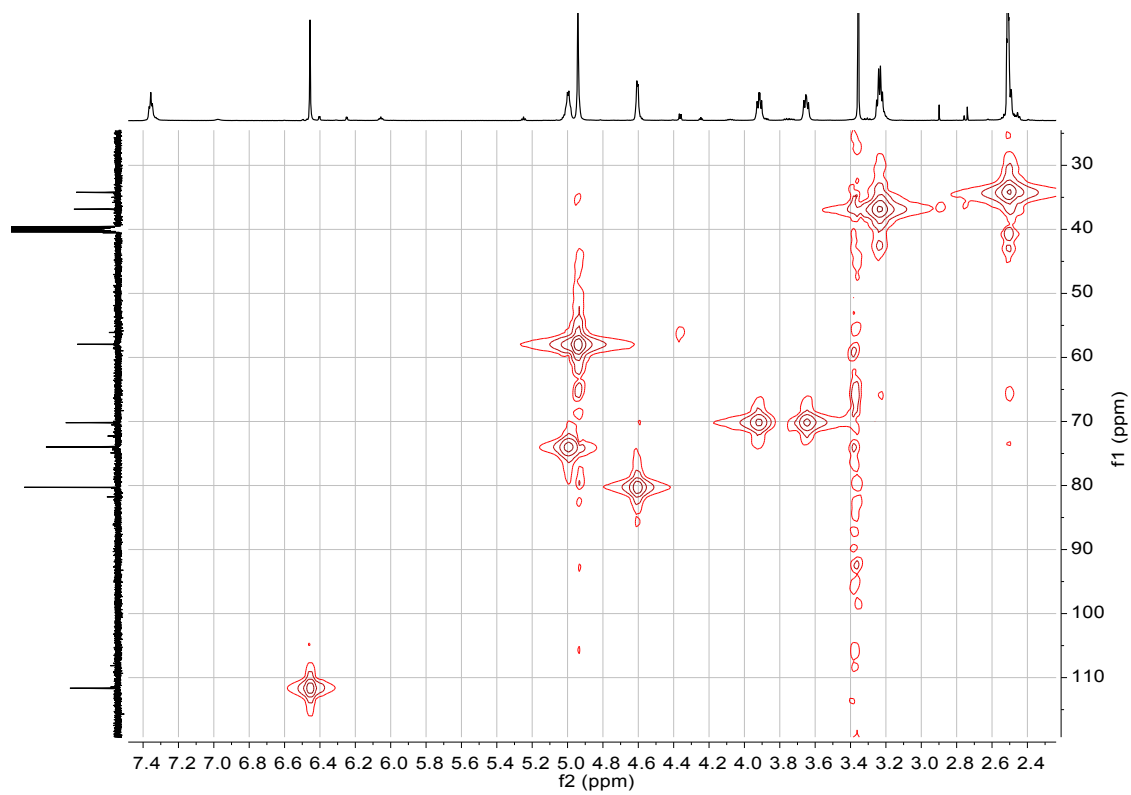


Figure S19: HMQC PU-IM (600 MHz, 150 MHz, DMSO- d_6)

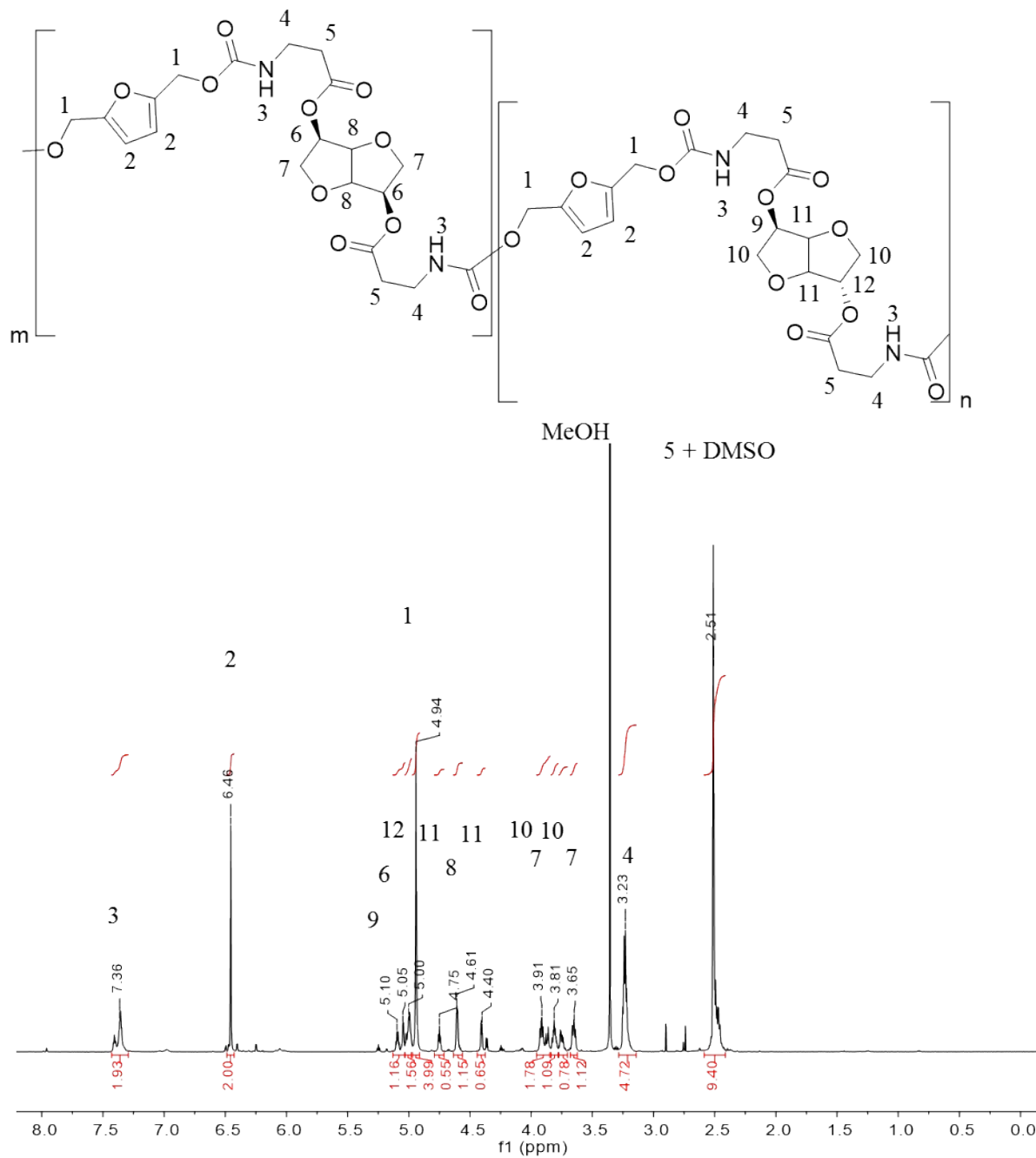


Figure S20: ¹H NMR PU-IS_{0.5}IM_{0.5} (600 MHz, DMSO-d₆).

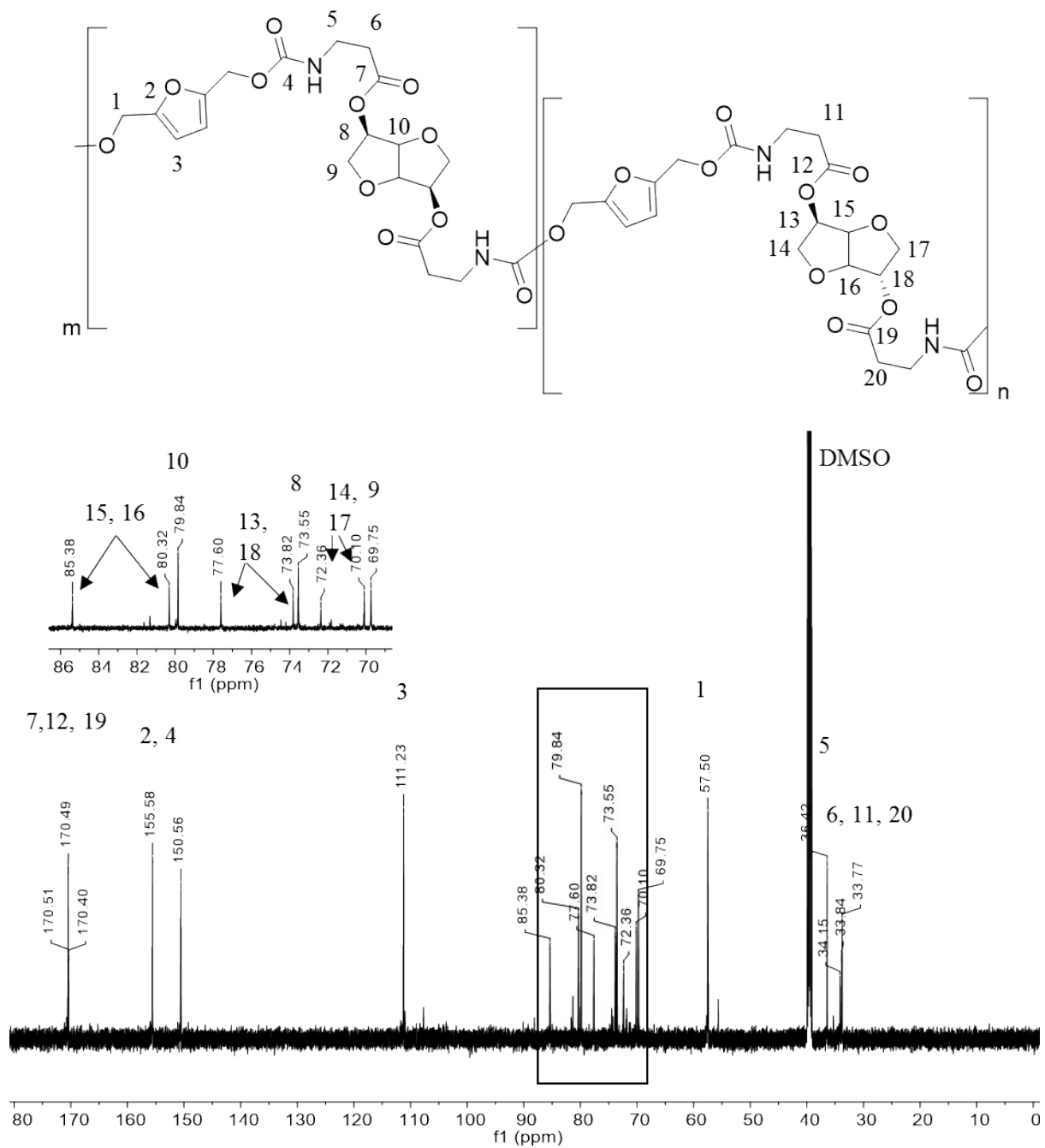


Figure S21: ¹³C NMR PU-IS_{0.5}IM_{0.5}. Inset shows region in black box expanded. (151 MHz, DMSO-d₆)

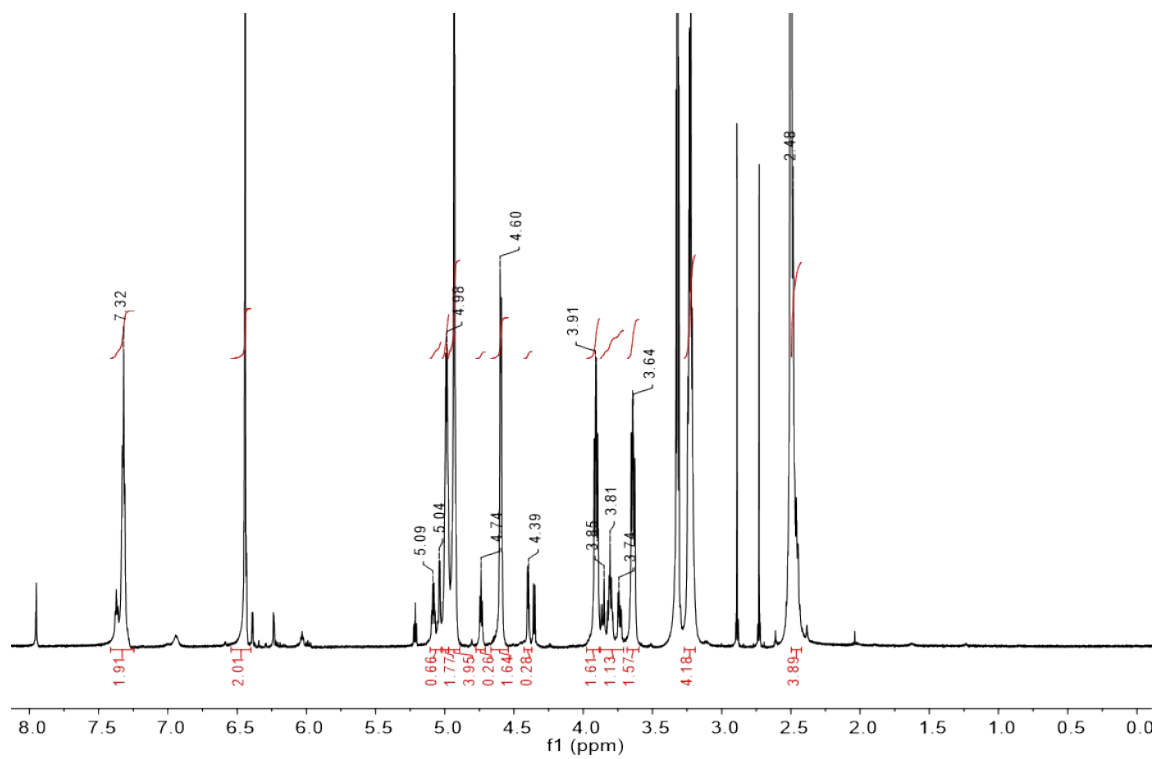


Figure S22: ^1H NMR PU-IS_{0.25}IM_{0.75} (600 MHz, DMSO-*d*₆).

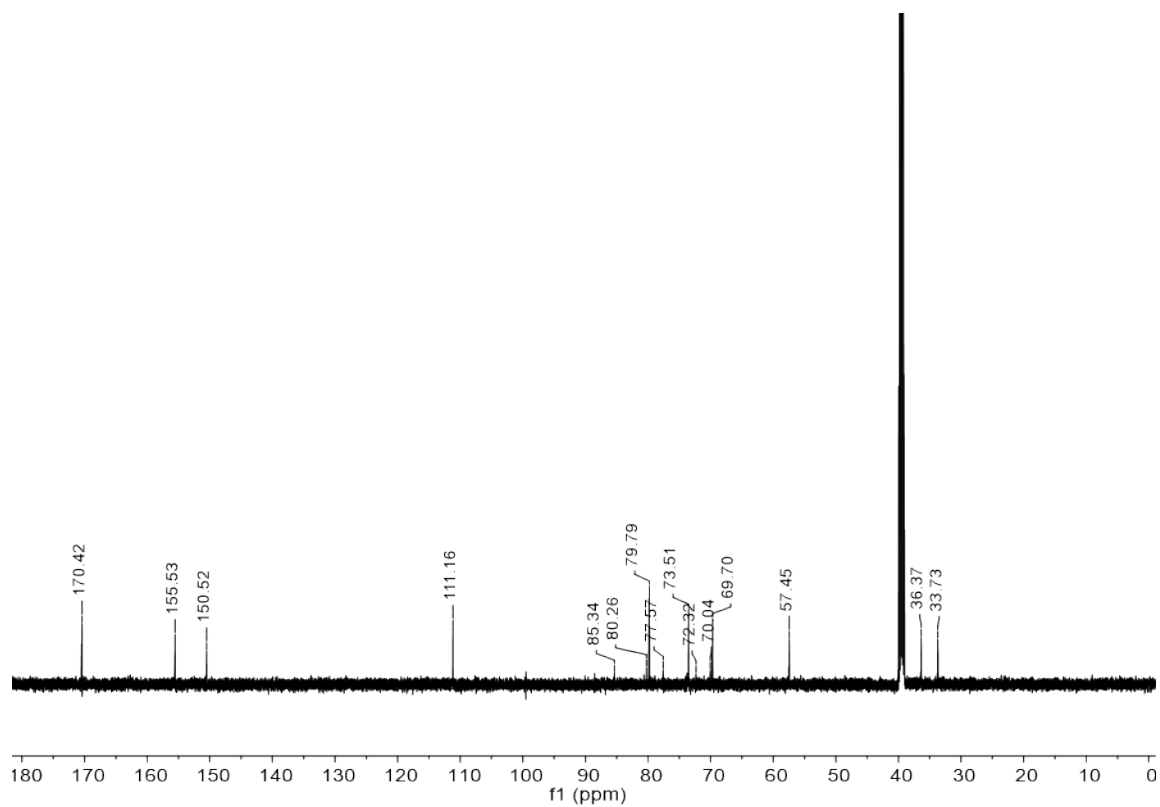


Figure S23: ^{13}C NMR PU-IS_{0.25}IM_{0.75}. (151 MHz, DMSO-*d*₆).

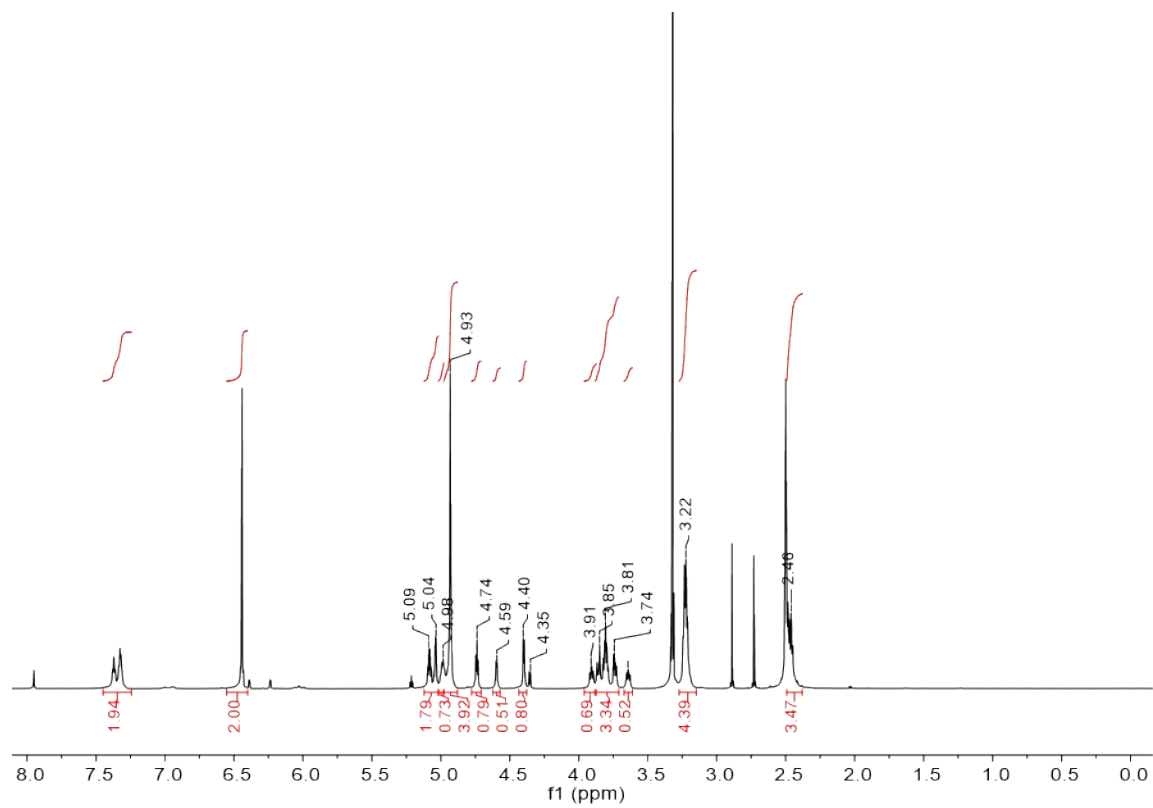


Figure S24: ^1H NMR PU-IS_{0.75}IM_{0.25}. (600 MHz, DMSO-*d*₆).

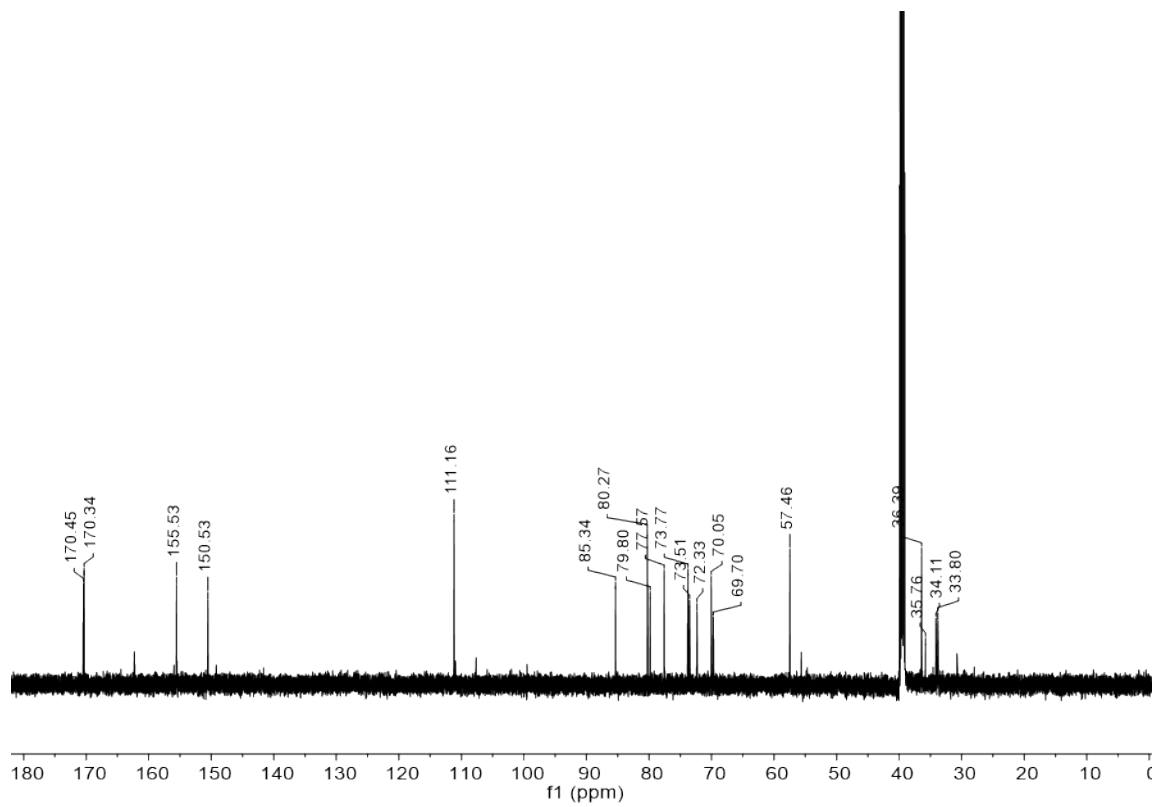


Figure S25: ^{13}C NMR PU-IS_{0.75}IM_{0.25}. (151 MHz, DMSO- d_6).

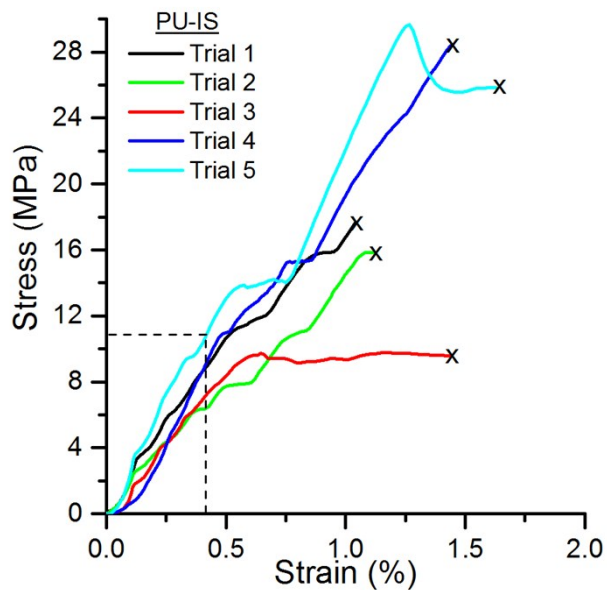


Figure S26: Stress-strain curve for sample PU-IS. Stress was applied uniaxially at a rate 50% of the original length in mm min^{-1} . Trial 4 and Trial 5 were taken as the representative toughest samples and averaged for Figure 4a. Dashed box indicates region used to calculate E .

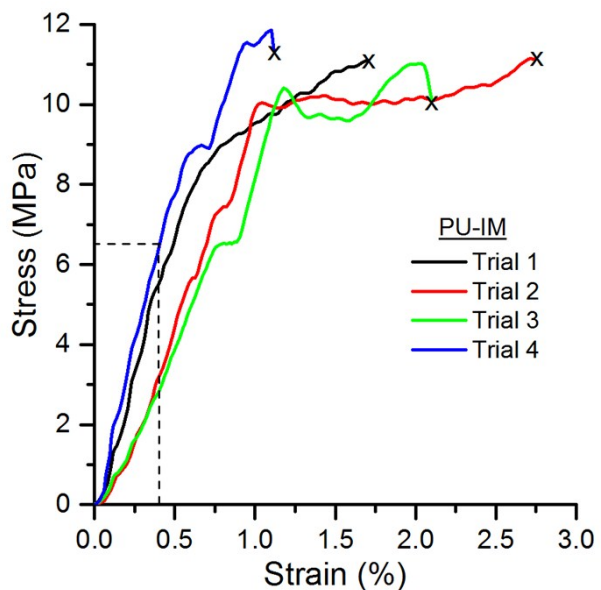


Figure S27: Stress-strain curve for sample PU-IM. Stress was applied uniaxially at a rate 50% of the original length in mm min^{-1} . Trial 1, Trial 2, and Trial 3 were taken as the representative toughest samples and averaged for Figure 4. Dashed box indicates region used to calculate E .

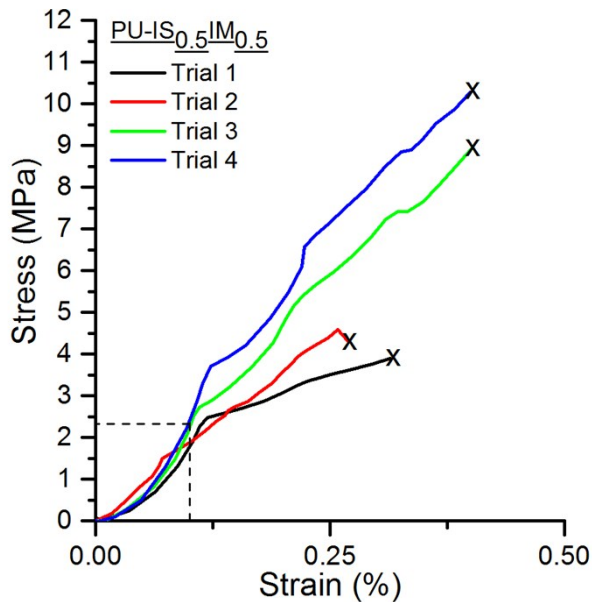


Figure S28: Stress-strain curve for sample PU-IS_{0.5}IM_{0.5}. Stress was applied uniaxially at a rate 50% of the original length in mm min⁻¹. Trials 3 and 4 were used as representative toughest samples and averaged for Figure 4. Dashed box indicates region used to calculate *E*.

Equation S1: Calculation for determining dn/dc for polyurethanes with varying stereochemistry

$$\frac{dn}{dc} = \left(\frac{dn}{dc}^{pure IS}\right)(X_{IS}) + \left(\frac{dn}{dc}^{pure IM}\right)(X_{IM})$$

Equation S2: Williams-Landel-Ferry (WLF) equation relating frequency factor (a_T) (Table S1) to *T*, using a reference temperature T_r of 120 °C.

$$\log(a_T) = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)}$$

Equation S3: In order to determine C_1 and C_2 , the WLF equation was modified to the following linear fit of $-\log(a_T)^{-1}$ vs $(T - T_r)^{-1}$, where the $C_1 = 1/y$ -intercept and $C_2 = C_1 * \text{slope}$

$$-\frac{1}{\log(a_T)} = \frac{C_2}{C_1} \left(\frac{1}{T - T_r} \right) + \frac{1}{C_1}$$

Equation S4: Calculation of molecular weight between entanglements (M_e) using the density (ρ), the plateau modulus (G_N°) (taken as the storage modulus (G') when $\tan \delta$ reaches a minimum along the ω axis), the universal gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and the reference temperature $T_{\text{ref}} = 120 \text{ }^\circ\text{C}$.

$$M_e = \frac{\rho RT}{G_N^\circ}$$

Density determined at $23 \pm 1 \text{ }^\circ\text{C}$ was adjusted to that predicted at $120 \text{ }^\circ\text{C}$ following the procedure outlined by Van Krevelen¹⁻², the steps are outlined in Equations S5-S7.

Equation S5: 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 S6: Calculation of the van der Waals volume (V_w)

$$V_w = \frac{V(23 \text{ }^\circ\text{C})}{1.6}$$

Equation S7: Molar volume at a given temperature T , where $T = T_{\text{ref}}$ ($120 \text{ }^\circ\text{C}$)

$$V(T) = V(23 \text{ }^\circ\text{C}) + 0.45 * 10^{-3}(T_g - 23 \text{ }^\circ\text{C})V_w + 1.0 * 10^{-3}(T - T_g)V_w$$

Table S2: Parameters used to calculate PU density at $120 \text{ }^\circ\text{C}$ in Equation S5-S7. Densities obtained were used in Equation S4.

| Sample | T_g ($^\circ\text{C}$) | ρ (23 $^\circ\text{C}$) (g cm^{-3}) | M_o (g mol^{-1}) | V (23 $^\circ\text{C}$) (cm ³ mol^{-1}) | V_w (cm ³ mol^{-1}) | ρ (120 $^\circ\text{C}$) (g cm^{-3}) |
|--|----------------------------|---|------------------------------|---|--|--|
| PU-IS | 51.5 | 1.37 | 468.42 | 341.9124 | 213.6953 | 1.30 |
| PU-IS _{0.5} IM _{0.5} | 41.8 | 1.32 | 468.42 | 354.8636 | 221.7898 | 1.25 |
| PU-IM | 40.24 | 1.27 | 468.42 | 368.8346 | 230.5217 | 1.20 |

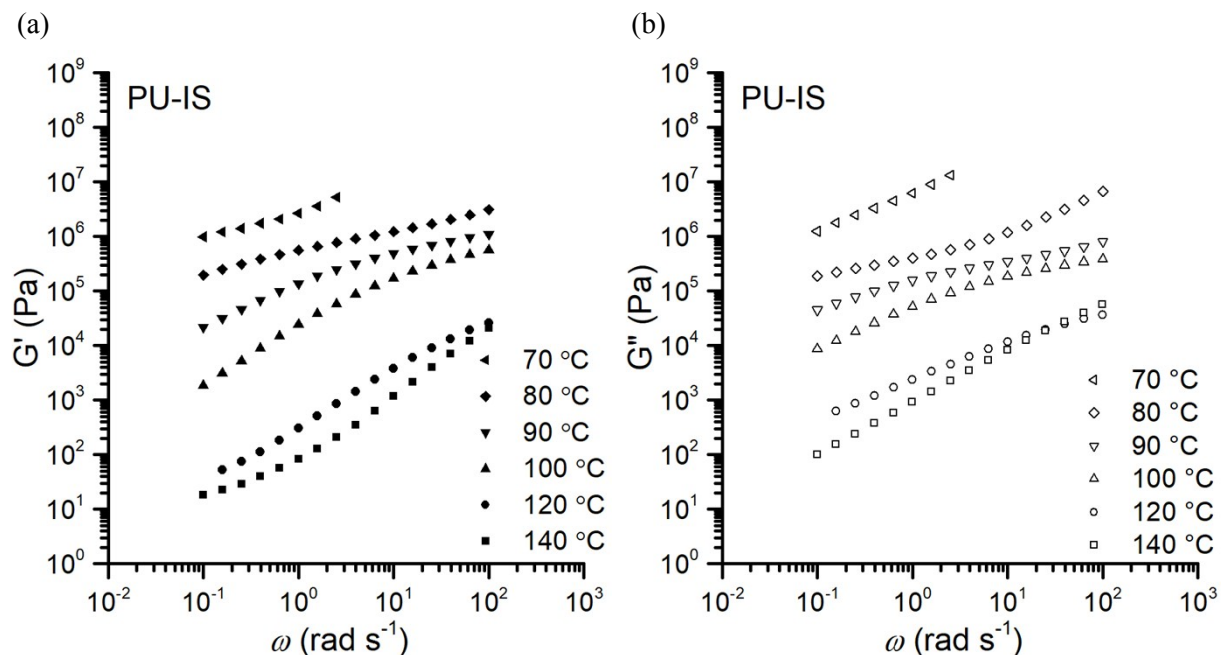


Figure S29: Frequency sweeps of (a) storage modulus (G') and (b) loss modulus (G'') for PU-IS at varying temperature within the linear viscoelastic regime used for TTS plots in Figure 4b.

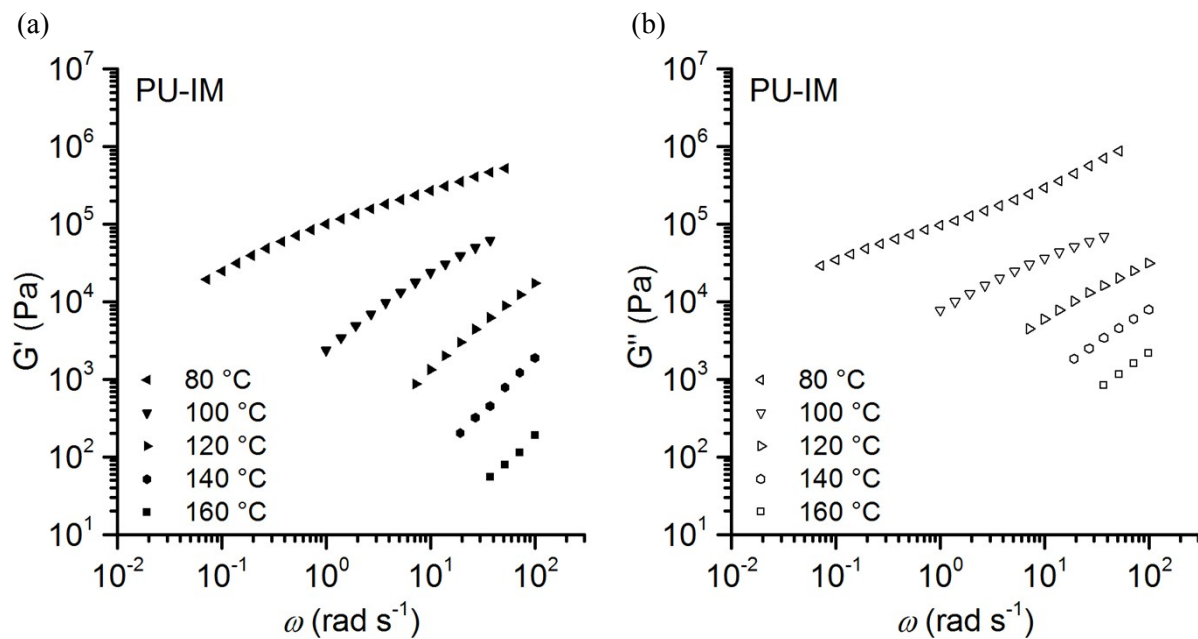


Figure S30: Frequency sweeps of (a) storage modulus (G') and (b) loss modulus (G'') for PU-IM at varying temperature within the linear viscoelastic regime used for TTS plot in Figure 4c.

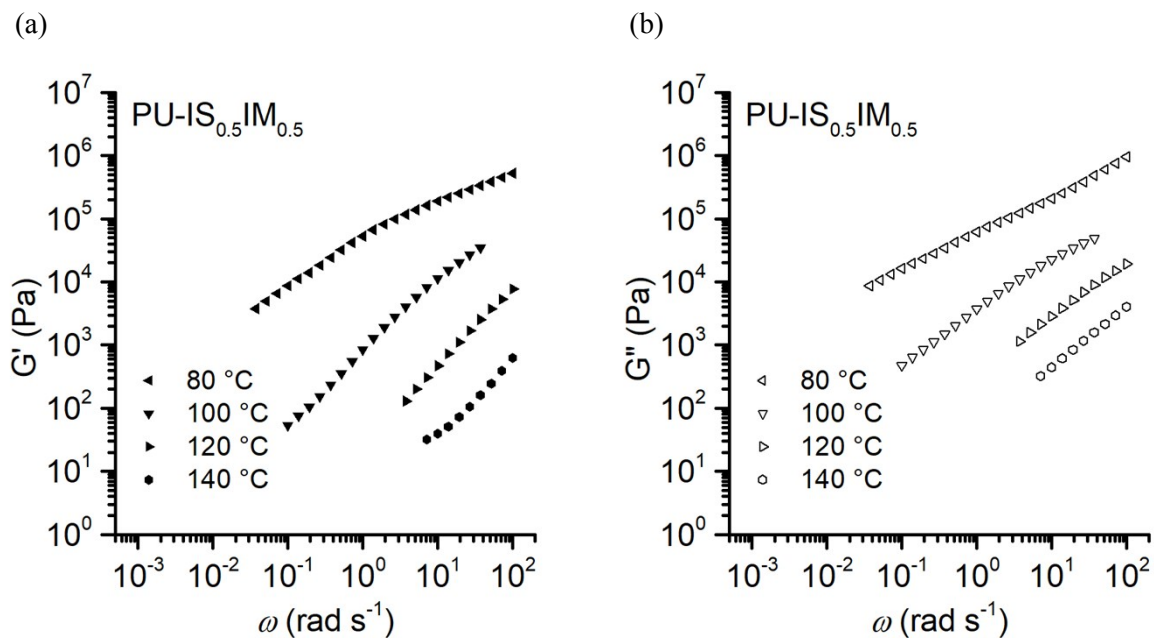


Figure S31: Frequency sweeps of (a) storage modulus (G') and (b) loss modulus (G'') for PU-IS_{0.5}IM_{0.5} at varying temperature within the linear viscoelastic regime used for TTS plot in Figure 4d.

Table S1: Strain values and shift factors (a_T) used for TTS master plots and WLF fitting.

| Sample | T (°C) | Strain (%) | a_T |
|--|--------|------------|--------|
| PU-IS | 70 | 0.05 | 600000 |
| | 80 | 0.1 | 7000 |
| | 90 | 0.5 | 500 |
| | 100 | 0.5 | 65 |
| | 120* | 1 | 1 |
| | 140 | 1 | 0.175 |
| PU-IS _{0.5} IM _{0.5} | 80 | 1 | 1950 |
| | 100 | 1 | 20 |
| | 120* | 1 | 1 |
| | 140 | 2 | 0.15 |
| PU-IM | 80 | 1 | 2000 |
| | 100 | 1 | 15 |
| | 120* | 2 | 1 |
| | 140 | 2 | 0.1 |
| | 160 | 3 | 0.023 |

*reference temperature (T_{ref})

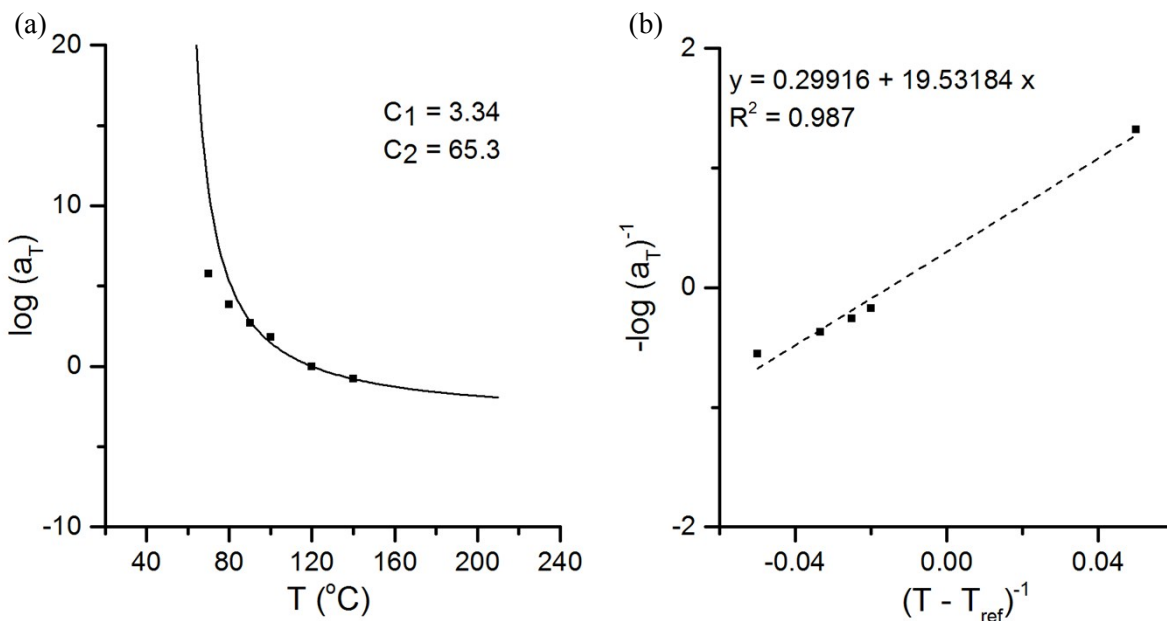


Figure S32: (a) Logarithmic shift factors for PU-IS vs T with $T_{\text{ref}} = 120$ $^{\circ}\text{C}$. Solid line is WLF equation using $C_1 = 3.34$ and $C_2 = 65.3$. (b) Linearized version of WLF equation plotting shift factors for PU-IS with $T_{\text{ref}} = 120$ $^{\circ}\text{C}$. C_1 is found by taking $1/y$ -intercept, and C_2 by taking slope $\times C_1$

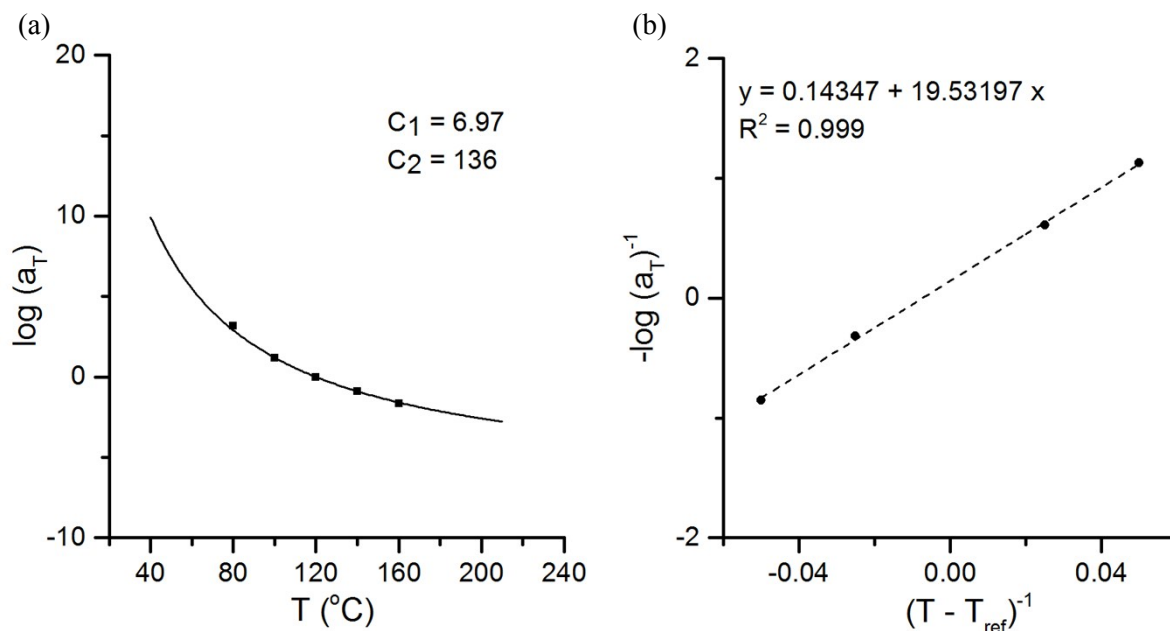


Figure S33: (a) Logarithmic shift factors for PU-IM vs T with $T_{\text{ref}} = 120$ $^{\circ}\text{C}$. Solid line is WLF equation using $C_1 = 6.97$ and $C_2 = 136$. Linearized version of WLF equation plotting shift factors for PU-IM with $T_{\text{ref}} = 120$ $^{\circ}\text{C}$. C_1 is found by taking $1/y$ -intercept, and C_2 by taking slope $\times C_1$

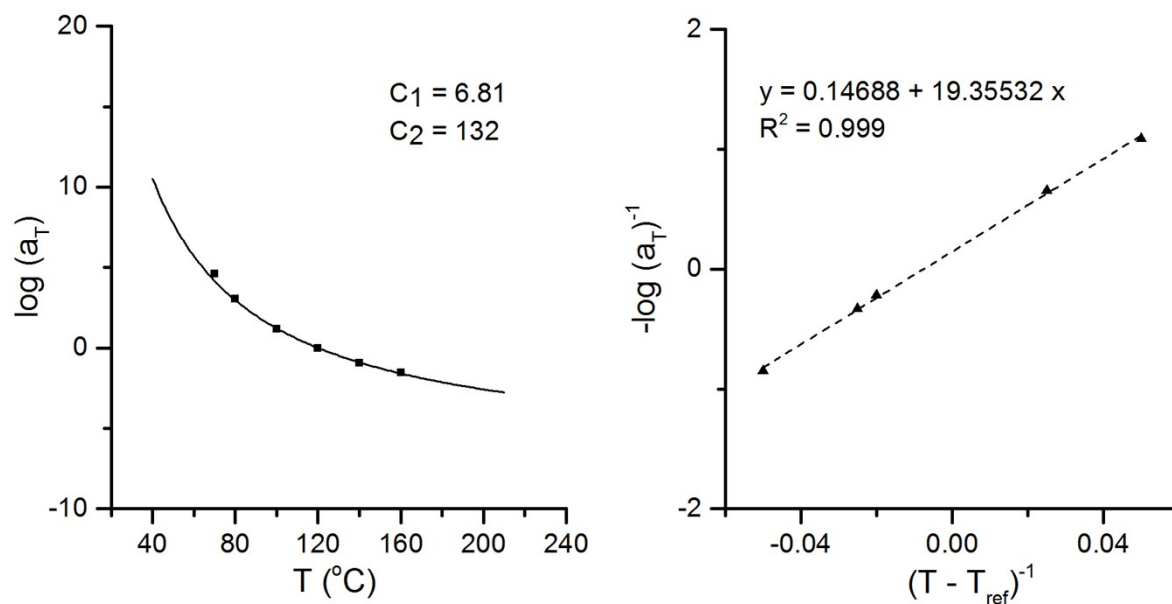


Figure S34: Logarithmic shift factors for PU-IS_{0.5}IM_{0.5} vs T with $T_{ref} = 120$ °C. Solid line is WLF equation using $C_1 = 6.81$ and $C_2 = 132$. Linearized version of WLF equation plotting shift factors for PU-IS_{0.5}IM_{0.5} with $T_{ref} = 120$ °C. C_1 is found by taking 1/y-intercept, and C_2 by taking slope $\times C_1$

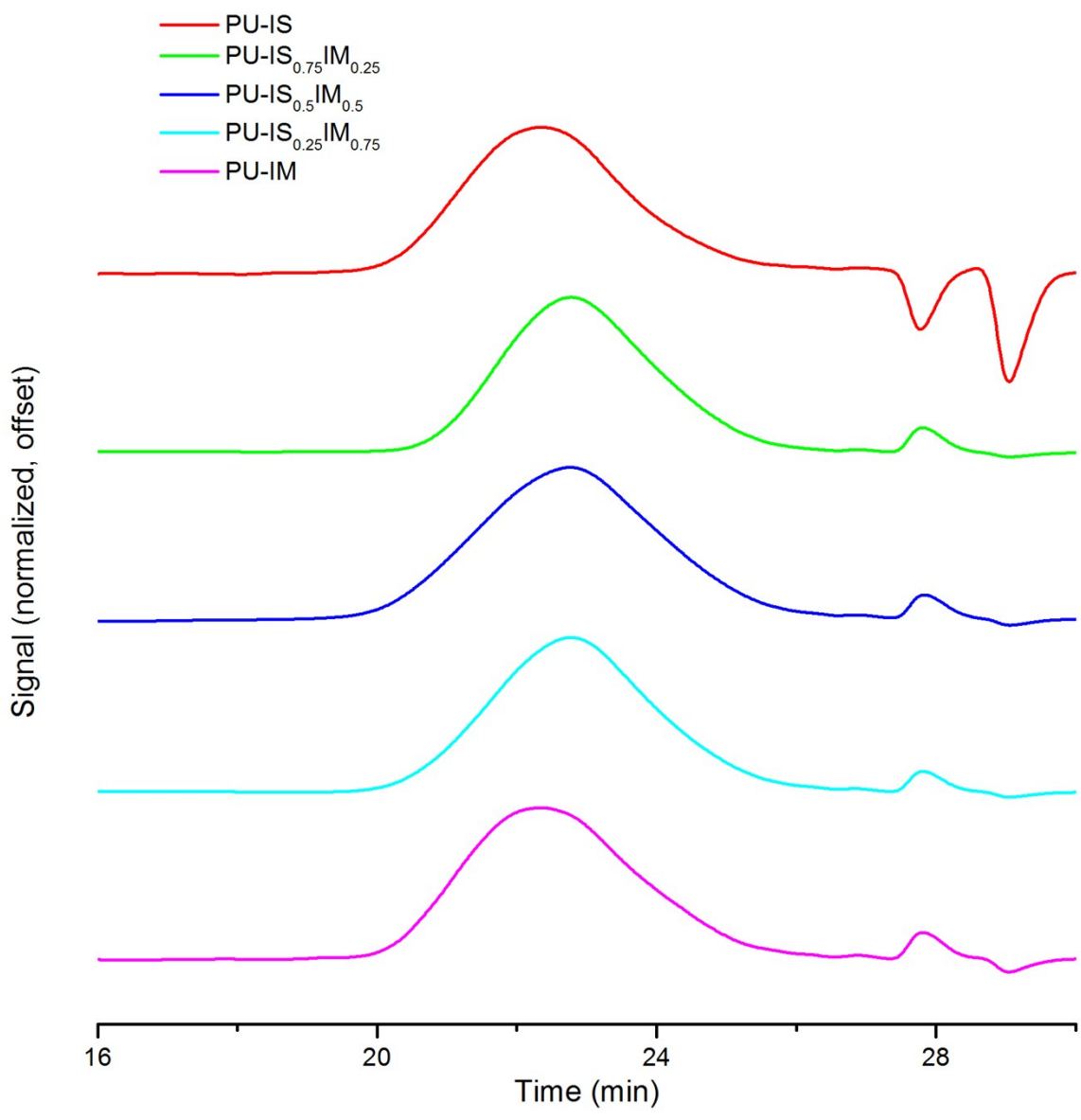
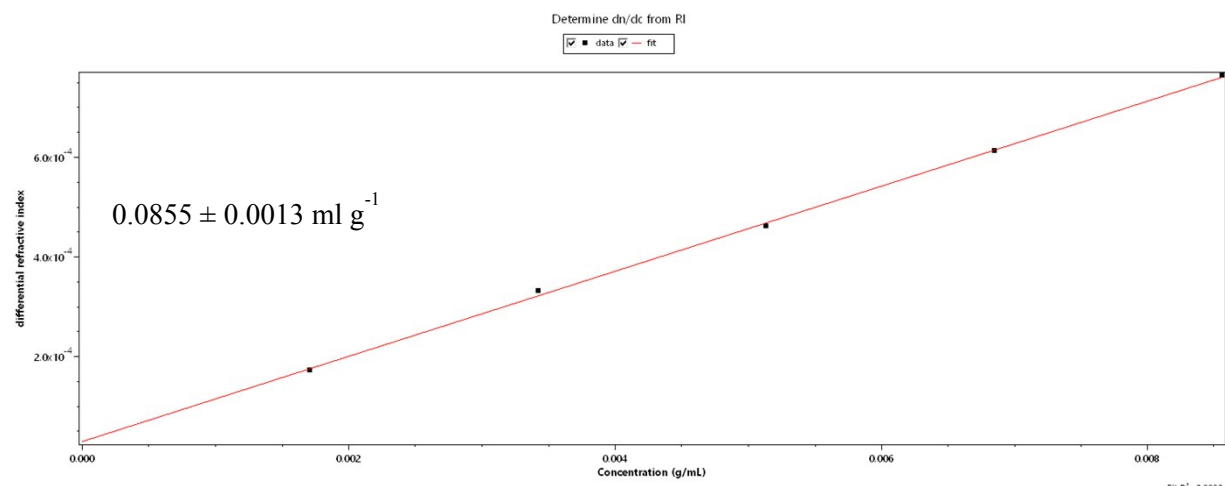
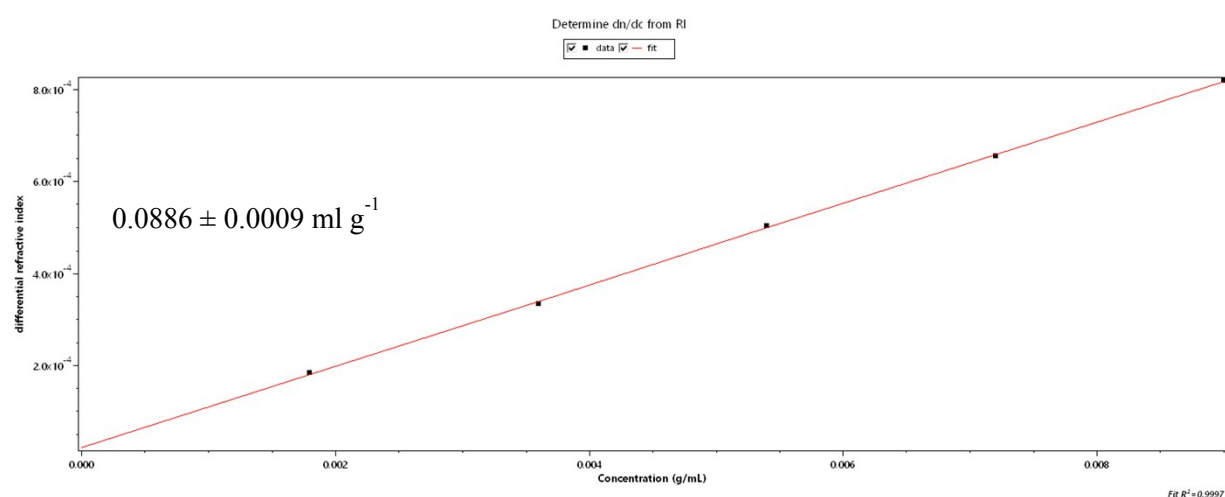


Figure S35: Normalized, offset, RI traces of polyurethanes obtained by SEC analysis. Samples were run at 25 °C in DMF (0.05 M LiBr).



| | Value |
|--------------------|----------------------|
| dn/dc | 0.0855 ± 0.0013 mL/g |
| Fit Degree | 1 |
| Percentage To Keep | 100 |
| Enabled Peaks | |

Figure S36: Linearized dn/dc determination for PU-IS obtained from RI detector generated by ASTRA software. Samples were dissolved in DMF (0.05 M LiBr stabilized) with known concentrations, and injected directly into the detector.



| | Value |
|--------------------|----------------------|
| dn/dc | 0.0886 ± 0.0009 mL/g |
| Fit Degree | 1 |
| Percentage To Keep | 100 |
| Enabled Peaks | |

Figure S37: Linearized dn/dc determination for PU-IM obtained from RI detector generated by ASTRA software. Samples were dissolved in DMF (0.05 M LiBr stabilized) with known concentrations, and injected directly into the detector.

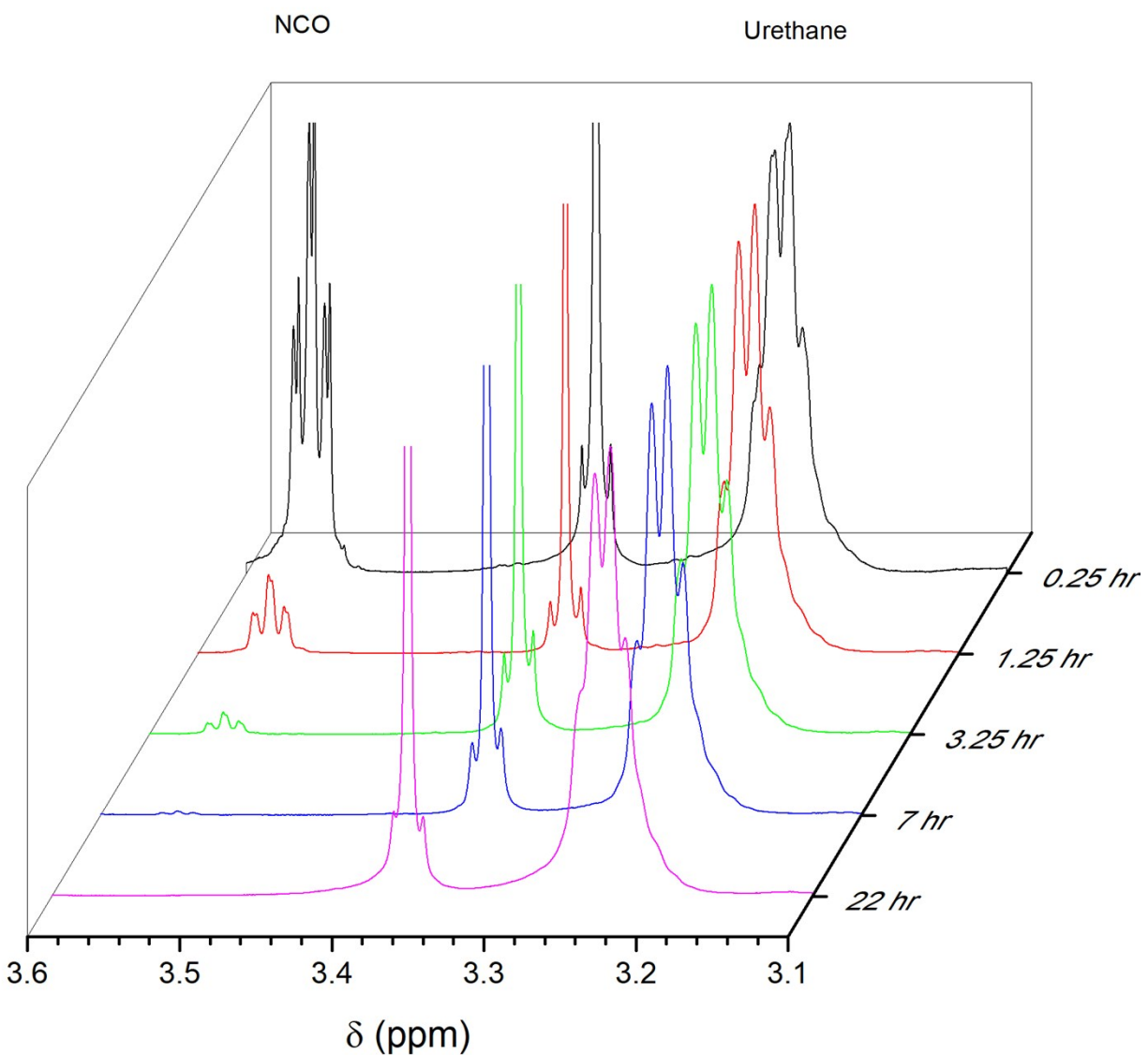


Figure S38: ^1H NMR time study of polymerization of ISBIP and BHMF, showing complete loss of the peak associated with the methylenes adjacent to the isocyanate at ~ 3.52 ppm.

Table S3: Polymerization conditions for each reported PU, showing the stoichiometric ratio of the monomers (r)

| Sample | % Yield | mmol BHMF | mmol ISBIP/IMBIP | r |
|--|---------|-----------|------------------|---------|
| PU-IM | 88 | 14.699 | 14.699 | 0.99997 |
| PU-IS _{0.25} IM _{0.75} | 66 | 11.803 | 11.804 | 0.99987 |
| PU-IS _{0.5} IM _{0.5} | 92 | 14.774 | 14.775 | 0.99993 |
| PU-IS _{0.75} IM _{0.25} | 82 | 14.763 | 14.765 | 0.99987 |

PU-IS 88 9.120 9.119 0.99996

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*, 7155-7164.