Supplementary Information

Sugar-based Polymers with Stereochemistry Dependent-Degradability and Mechanical properties

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Materials and methods

All manipulations of air sensitive compounds were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All compounds, unless otherwise indicated, were purchased from commercial sources and used as received. The following chemicals were vacuum distilled prior to use and stored in Young’s tapped ampoules under N\(_2\): 1,8-octanedithiol (Sigma-Aldrich, ≥ 97%). All solvents and chemicals used for recrystallisation were used as received. All polymer reactions were precipitated into methanol and dried in vacuo at ambient temperature for 24 h and then at 100 °C overnight (ca. 16 h). After processing, all samples were annealed for 3 d at ambient temperature before analysis.

Characterization techniques

All NMR spectroscopy experiments were performed at 298 K on a Bruker DPX-400 NMR instrument equipped operating at 400 MHz for \(^1\)H (100.57 MHz for \(^{13}\)C). \(^1\)H NMR spectra are referenced to residual protic solvents (CDCl\(_3\) at δ = 7.26 ppm, DMSO–d\(_5\) at δ = 2.50) and \(^{13}\)C NMR spectra are referenced to the residual solvent signal (CDCl\(_3\) at δ = 77.16 ppm, δ = 39.52 for DMSO–d\(_6\)). The resonance multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

Mass spectrometry was performed by University of Birmingham School of Chemistry on a Waters GCT Premier using electrospray ionization and on Waters Xevo G2-XS using chemical H+ ionization.

FTIR spectroscopy was carried out using an Agilent Technologies Cary 630 FTIR spectrometer. 16 Scans from 600 to 4000 cm\(^{-1}\) were taken at a resolution of 2 cm\(^{-1}\), and the spectra were corrected for background absorbance.

SEC measurements were performed in CHCl\(_3\) on an Agilent 1260 Infinity II Multi-Detector GPC/SEC System fitted with RI, ultraviolet (UV, λ = 309 nm), and viscometer detectors. The polymers were eluted through an Agilent guard column (PLGel 5 μM, 50 × 7.5 mm) and two Agilent mixed-C columns (PLGel 5 μM, 300 × 7.5 mm) using CHCl\(_3\) (buffered with 0.5% NEt\(_3\)) as the mobile phase (flow rate = 1 mL·min\(^{-1}\), 40 °C). Number average molecular weight (\(M_n\)), weight average molecular weight (\(M_w\)) and dispersity (\(D_M = M_w/M_n\)) were determined using Agilent GPC/SEC software (vA.02.01) against a 15-point calibration curve (\(M_p = 162 – 3,187,000\) g·mol\(^{-1}\)) based on polystyrene standards (Easivial PS-M/H, Agilent).

Thermal characterization

Determination of the thermal characteristic of the polymer were carried out using a STARe system DSC3 with an auto-sampler (Mettler Toledo, Switzerland). Disc shapes measuring 5 mm in diameter and 0.4 – 0.6 mm in thickness and weighing between 9 – 14 mg were cut from annealed polymer films. Thermograms were obtained in 40 µL aluminum pans from -50 to 200 °C (0 to 280 °C for Nylon-6) at a heating rate of 10 K·min\(^{-1}\) for two heating/cooling cycles unless otherwise specified. The glass transition temperature (\(T_g\)) was determined by the minimum of the first derivative in the second heating cycle of DSC. Total enthalpy of melting (\(\Delta H_m\)) was calculated from integration and normalization of all endothermic peaks present.

Annealing studies were performed using a DSC3 (Mettler Toledo, Switzerland) on a heat pressed film of IIPU. The sample was heated from 25 °C to 200 °C at a heating rate of 10 K·min\(^{-1}\) to erase the thermal history. The sample was then cooled to 25 °C and isothermally annealed for 3 hours before cooling to -50 °C and then heated to 200 °C at a heating rate of 10 K·min\(^{-1}\) to measure the enthalpy of melting of the annealed sample. This procedure was then repeated with an initial annealing temperature of 50 °C.

Thermal degradation was quantified using a Q550 Thermogravimetric analyzer (TA instruments). Thermograms were recorded under an N\(_2\) atmosphere at a heating rate of 10 K·min\(^{-1}\) from 25 to 600 °C. Decomposition temperatures were reported at the 5% weight loss temperature (\(T_d, 5\%\)).

Mechanical characterization

Uniaxial tensile testing was performed using a Testometric M350-5CT universal mechanical testing instrument fitted with a load cell of 100 kN. Samples were prepared into thin polymer films using
Specac Atlas™ Manual Hydraulic Press 15T fitted with Specac heated plates.* The polymer was added into a 40 × 50 × 0.50 mm stainless steel mold and placed into pre-heated press at 160 °C. The sample was heated for 10 min (with no pressure) before degassing 5 × (500 kg pressure/release). Next, 4000 kg pressure was applied, and the sample was held at 160 °C for 5 min before cooling to ~ 25 °C under the same pressure. Film samples were visually inspected for deformation and bubbles before annealing for 3 days at 22 °C. Finally, dumbbell shaped samples were cut using custom ASTM Die D-638 Type 5. Each specimen was clamped into the tensile holders and subjected to an elongation rate of 10 mm-min⁻¹ until failure. All tensile tests were repeated at least 5 times (unless otherwise indicated), and an average of the data was taken to find the ultimate tensile stress and strain. Data was analyzed using winTest™ Analysis software (v.5.0.34) and OriginPro® software. *Data obtained for mechanical recycling was performed using films that were fabricated using an automated Carver CMG 30H-12 ASTM floor standing model. Statistical analysis between samples was performed using an ordinary single factor ANOVA test.

Cyclic tensile recovery experiments were performed on annealed dumbbell shaped samples of IMPU and stretched to roughly ~300%, then the sample was allowed to relax for 30s at 22 °C. Images were taken at each stage and the strain was quantified using imageJ software.

Rheology experiments were performed on an Anton Paar MCR 302 using a PP8 geometry on discs (8 × 1 mm) cut out of films fabricated using a Specac Atlas™ Manual Hydraulic Press 15T fitted with Specac heated plates (as detailed in tensile testing method). Temperature was controlled with a P-PTD 200/AIR Peltier and a P-PTD 200 hood. Frequency sweeps were performed at 1% strain from 0.1 to 100 rad·s⁻¹ at 5 °C intervals between the temperatures of 140 °C to 170 °C and 100 °C to 130 °C for IMPU. G’ and G” of IIIPU and IMPU were overlayed to a single spectrum at a reference temperature of 130 °C by applying a Williams-Landel-Ferry (WLF) time-temperature superposition. Molecular entanglement was extracted by fitting polydisperse double reptation theory in the REPTATE software package.¹ Molecular weights obtained from SEC, were discretized to 20 values per decade and used as theory input. The adjustable parameters in the fitting were $G_e$ (entanglement modulus), $M_e$ (entanglement molecular weight), $\tau_e$ (Rouse time of one entangled segment) and the value of $M_0$ was kept to a value of 0.001 kg·mol⁻¹ as recommended.¹

Atomic force microscopy (AFM)

Atomic Force Microscopy was performed on a JPK Nanowizard 4 system at room temperature in the supplied acoustic enclosure and vibration isolation using Nanosensor PPP-NCHAU'D tips with a force constant of around 42 N·m⁻¹. For data acquisition and handling Nanowizard Control and Data Processing Software V.6.1.117 in QI mode with a setpoint of 30 nN was used. Adhesion was calculated by first subtracting the baseline from each force curve and then identifying the lowest point of the retraction force curve. Slope, a proxy for the Young’s modulus of the material, was taken as the average slope of the steepest segment of the approach force curve. Sample were prepared via melt pressing samples onto glass slides at 160 °C.

Contact angle measurements

Contact angle between water and the polymer surface was measured using a Krüss DSA25S drop-shape analyser (Hamburg, Germany) at 20 °C. Melt-pressed (at 160 °C) polymer films were subjected to 5 μL sessile drops of deionised water and measured using Youngs–Laplace fitting. Contact angles were reported as the average of 5 measurements and standard deviation is shown as the uncertainty.

Molecular dynamics simulation details

Atomistic molecular dynamics simulations were performed using the General Amber Force Field² (GAFF) to model the isohexide-containing polyurethanes. The forces on the atoms were calculated by differentiating the potential energy of the system, which consisted of bonded (bonds, angle, dihedral, and improper potentials) interactions as well as nonbonded interactions (van de Waals and electrostatic):
$$U = \sum_{\text{Bonds}} k_r (r - r_{eq})^2 + \sum_{\text{Angles}} k_\theta (\theta - \theta_{eq})^2$$
$$+ \sum_{\text{Dihedrals}} k_d [1 + \text{d}\cos(n\phi)]$$
$$+ \sum_{i<j} \left( 4\epsilon_{ij} \left( \left( \frac{a}{r_{ij}} \right)^{12} - \frac{a}{r_{ij}} \right) + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right)$$  \hspace{1cm} (S1)

where $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$ is dielectric permittivity of the vacuum, $\varepsilon$ is a medium relative dielectric constant.

In GAFF, the van de Waals interactions are represented by the Lennard-Jones (LJ) potentials with parameters given for each homogeneous atomic pairs ($r_{ij}$ and $\varepsilon_{ij}$), while the parameters for heterogeneous pairs are determined as $r_{ij} = r_i + r_j$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. The LJ-potential is truncated at a cutoff distance of 10 Å. The weighting coefficient for the 1-4 interaction was set to 0.5 for the LJ-interactions and 0.833 for the Columbic interactions. Partial charge distributions were obtained from DFT calculations using B3LYP 6-31G* (d,p) basis set for AM1 optimized structures (Figure S40). These simulations were done by using Gaussian 09. The interaction parameters for non-bonded/bonded interactions are summarized in Table S6. Each polymer chain has $n=16$ repeat units. Information about macromolecular structure (list of bonds, angles, dihedrals, improper dihedrals) was generated by Topotools plugins in VMD.\(^3\)

**Simulations of chain deformation**

The two ends of each polymer chain were connected across the periodic boundary along x direction forming a loop representing an infinitely long polymer chain. There were two identical chains in the periodic simulation box with equilibrium dimensions $L_x=80$ Å and $L_y=L_z=40$ Å. The system was equilibrated for 5000 ns. After equilibration, two polymer chains adopted a bundle-like conformation. The equilibration step followed by simulations of chain deformation. During these simulations, simulation box was deformed along x-direction at a constant strain rate $2.5 \times 10^{-6}$ fs\(^{-1}\). The system temperature was maintained by coupling the system to the thermostat applied in y and z directions. All simulations were performed using the following setup: PPPM\(^4,5\) method for calculations of the electrostatic interactions with targeted accuracy $10^{-4}$, vacuum dielectric constant $\varepsilon = 1.0$, $T = 300$ K, Langevin thermostat (damping parameter 10 fs), and time step $dt = 0.5$ fs. All simulations were performed using LAMMPS with GPU acceleration.\(^6\)

**Simulations of IIPU, IMPU, copolymers and physical blends bulk systems**

The bulk systems of pure polymer components, polymer blends and copolymers were prepared by implementing the following procedure: (i) 75 polymer chains with degree of polymerization $n = 16$ were randomly distributed in a cubic box with the side length of 300 Å and with partial charges on the atoms switched off; (ii) the simulation box was slowly compressed to achieve equilibrium system density $\rho \approx 1$ g·cm\(^{-3}\) over time 1.0 ns at constant temperature $T = 600$ K; (iii) after achieving required density, the system was relaxed for 1.0 ns under NVT ensemble conditions; (iv) with partial charges on the atoms switched on, the system was relaxed for 1.0 ns at fixed volume and temperature; (v) system was annealed to room temperature, $T = 300$ K, during 1.0 ns time interval; (vi) this followed by NPT ensemble simulation run lasting 5 ns with target temperature $T = 300$ K and pressure $P = 1.0$ atm. Data collection was done during additional 2 ns long simulation run under NPT ensemble conditions. All simulations were performed using LAMMPS with GPU acceleration.\(^6\) The final system densities are summarised in Table S4.

The specific surface area, $a$, was calculated as a ratio of the surface area, $A_{\text{interface}}$, of the interface between the isoidide and isommanide regions to the total system volume $V_{\text{sample}}$:

$$a = \frac{A_{\text{interface}}}{V_{\text{sample}}}$$

for the copolymer melts and polymer blends. The interfacial area was determined by calculating the area of interface between 3D density distribution of atoms belonging to IMPU and IIPU (or vice versa) assigned to the discrete grid points. The data are summarized in Table S5.
Physical Degradation Studies

Accelerated degradation studies were conducted under conditions previously reported by Lam et al.\textsuperscript{7} Polymer films were annealed for 3 days and then cut into “degradation disks” (ca. 0.1 g) and subjected to 1 M aq. NaOH at 25 °C. The disks were placed in individual vials containing 20 mL of the corresponding solution and incubated at 25 °C with constant agitation at 60 rpm. The surfaces of the disks were dried in order to remove excess water before the weight was measured periodically using an analytical balance.

Quantitative Degradation Studies

Hydrophobicity (i.e. LogP/SA values) was calculated with Materials Studio 2019. LogP values were extracted from the QSAR menu using the ALogP98 option. Connolly surface area (SA) was calculated with a 1.40 Å probe after conducting a Molecular Dynamics simulation of molecular models. The Forcite Geometry Optimization employed a Smart algorithm and COMPASS II forcefield to minimize the energy below certain specifications. Convergence tolerance for the Smart algorithm included a 1.0 x 10\textsuperscript{-3} kcal/mol energy convergence, a 0.005 kcal/mol/Å force convergence, and a 5.0 x 10\textsuperscript{-5} Å displacement convergence. To improve accuracy of LogP/SA values, multiple models ranging from 10, 12, and 14-monomer units were averaged.
Synthetic procedures

Overview for the 3-step synthesis of isoidide from isomannide

Figure S1. Synthetic pathway from isomannide to isoidide. Adapted from a previous method.

Synthesis of isomannide tosylate

A 250 mL round bottom flask was charged with isomannide (68.4 mmol, 10.0 g, 1.0 equiv), triethylamine (171.1 mmol, 23.8 mL, 2.5 equiv), dimethylaminopyridine (6.8 mmol, 0.84 g, 0.1 equiv) and dichloromethane (100 mL). The reaction mixture was cooled to 0 °C and then p-toluenesulfonyl chloride (143.7 mmol, 27.4 g, 2.1 equiv) was added portion-wise over several minutes. After the addition was complete, the reaction was stirred at 22 °C overnight (ca. 16 h). The mixture was transferred a 500 mL separatory funnel and washed with 1 M HCl (1 × 50 mL), water (2 × 50 mL), NaHCO₃ (1 × 50 mL) and brine (1 × 50 mL). The remaining organic phase was dried with MgSO₄ and concentrated in vacuo to afford an off-white solid (60.3 mmol, 27.4 g, 88% yield). The crude product was recrystallized in ethanol to produce a white crystalline solid (60.3 mmol, 27.4 g, 88% yield).

1H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.76 (m, 4H), 7.38 – 7.30 (m, 4H), 4.84 (dddd, J = 7.7, 6.7, 3.8, 1.5 Hz, 2H), 4.50 – 4.43 (m, 2H), 3.91 (dd, J = 9.6, 6.7 Hz, 2H), 3.72 (dd, J = 9.5, 7.6 Hz, 2H), 2.45 (s, 6H).

13C NMR (101 MHz, Chloroform-d) δ 145.46, 133.14, 130.07, 128.13, 80.07, 77.95, 70.23, 21.85. HRMS (TOF-MS+ El) (m/z): [M]+ calculated for C₂₀H₂₂O₈S₂, 454.0756; found, 454.0770.

Synthesis of isoidide acetate

An oven-dried 500 mL 2-neck round bottom flask was charged with isomannide tosylate (66.0 mmol, 30.0 g, 1.0 equiv), potassium acetate (396.0 mmol, 38.9 g, 6.0 equiv) and 100 mL anhydrous DMF. The reaction was heated to 140 °C and checked by TLC after 4 h to reveal remaining tosylate starting material. Another portion of potassium acetate (15.0 g) was added and the mixture was stirred overnight (ca. 16 h total) after which TLC analysis revealed complete consumption of the tosylate compound. Note: we observed batch-to-batch variability for complete consumption of starting material ranging from 2 h at 130 °C to 24 h at 140 °C. The reaction was poured into 100 mL ice-water while it was warm (ca. 60 – 80 °C) and then transferred to a 500 mL separatory funnel. The mixture was extracted with EtOAc (4 × 75 mL) and the combined organic fractions were washed with water (5 × 50 mL), 5 % LiCl (5 × 50 mL) and brine (1 × 50 mL). The resultant organic phase was dried over MgSO₄ and concentrated in vacuo to afford an off-white solid (60.3 mmol, 27.4 g, 88% yield). The crude product was recrystallized in ethanol to produce a white crystalline solid (24.5 g, 79%).

1H NMR (400 MHz, Chloroform-d) δ 5.27 – 5.13 (m, 2H), 4.63 (s, 2H), 4.00 – 3.84 (m, 4H), 2.08 (s, 6H).

13C NMR (101 MHz, Chloroform-d) δ 170.09, 85.50, 77.74, 72.72, 21.06. HRMS (TOF-MS) (m/z): [M + H]+ calculated for C₁₀H₁₄O₆+ H, 231.0869; found, 231.0872.

Synthesis of isoidide

An oven-dried 100 mL 2-neck round bottom flask was charged with isoidide acetate (60.8 mmol, 14.0 g, 1.0 equiv), 50 mL anhydrous MeOH, and sodium methoxide (25 wt% solution in methanol) (5 mL, ~ 0.33 equiv). The reaction was stirred at 22 °C for 24 h and checked by TLC to confirm consumption of the acetate. Dowex® 50W X8 (3.0 g) was added and the mixture was stirred for 24 h. The reaction mixture was filtered into a 100 mL round bottom flask and the DOWEX resin was rinsed with MeOH (10 mL) and concentrated in vacuo to reveal a viscous oil. The oil was further dried overnight (ca. 16 h) at 100 mTorr pressure to afford a white solid (8.4 g, 95%) that was used without further purification.

1H NMR (400 MHz, DMSO-d₆) δ 5.13 (d, J = 3.7 Hz, 2H), 4.31 (s, 2H), 4.02 (td, J = 3.5, 1.3 Hz, 2H), 3.61 (qd, J = 9.4, 2.4 Hz, 4H).
NMR (101 MHz, DMSO-d6) δ 87.14, 74.76, 74.01. HRMS (TOF-MS-ES+) (m/z): [M]+ calculated for C₁₈H₂₄O₁₀N₂+H, 429.1509; found, 429.1504.

Synthesis of isoidide-urethane monomer

A 250 mL round bottom flask was charged with isoidide (27.3 mmol, 4.0 g, 1.0 equiv), 2-isocyanatoethyl acrylate (66.2 mmol, 9.34 g, 2.4 equiv), 50 mg BHT (to inhibit radical crosslinking) and 50 mL THF. Dibutyltin dilaurate (0.10 mmol, 61.1 μL, 0.002 equiv) was added in one portion causing an exotherm. After the exotherm, the reaction was stirred at 22 °C overnight (ca. 16 h) and checked by TLC to confirm consumption of isoidide. Approximately half of the solvent volume was removed in vacuo causing some precipitate to form. The reaction was diluted with 200 mL of cyclohexane and stirred for 1 h causing more precipitate to form. The precipitate was filtered and washed with cyclohexane (2 × 100 mL) to afford a white solid. The crude product was recrystallized from a mixture of cyclohexane and 50 mL THF. Dibutyltin dilaurate (0.16 mmol, 97.3 μL, 0.006 equiv) was added in one portion causing an exotherm. The mixture stirred at 22 °C overnight (ca. 16 h) and then diluted to approximately 50 mL with CHCl₃. The thiol was quantitatively transferred to the round bottom flask containing isohexide-urethane monomer using CHCl₃ (11 mL) for a final monomer concentration of ~0.5 M. The reaction mixture was cooled to −10 °C in a brine ice-bath and dimethylphenylphosphine (8.0 μL, 0.56 mmol, 0.01 equiv) was injected into one portion causing an exotherm. After the exotherm, the reaction was stirred at 22 °C for 3 h and then diluted to approximately 50 mL with CHCl₃. The polymer solution was precipitated into methanol and dried in vacuo at ambient temperature for 24 h and then at 100 °C overnight for ca. 16 h.

Synthesis of isomannide-urethane monomer

A 250 mL round bottom flask was charged with isomannide (51.3 mmol, 7.5 g, 1.0 equiv), 2-isocyanatoethyl acrylate (123.1 mmol, 15.9 g, 2.4 equiv), 50 mg BHT (to inhibit radical crosslinking), and 50 mL THF. Dibutyltin dilaurate (0.16 mmol, 97.3 μL, 0.006 equiv) was added in one portion to the reaction mixture, causing a mild exotherm. The mixture stirred at 22 °C overnight (ca. 16 h) and then diluted to approximately 50 mL with CHCl₃, causing some precipitate to form. The mixture stirred at 22 °C overnight (ca. 16 h) causing a mild exotherm. The mixture stirred at 22 °C overnight (ca. 16 h) and then diluted to approximately 50 mL with CHCl₃. The thiol was quantitatively transferred to the round bottom flask containing isohexide-urethane monomer using CHCl₃ (11 mL) for a final monomer concentration of ~0.5 M. The reaction mixture was cooled to −10 °C in a brine ice-bath and dimethylphenylphosphine (8.0 μL, 0.56 mmol, 0.01 equiv) was injected in one portion causing an exotherm. After the exotherm, the reaction was stirred at 22 °C for 3 h and then diluted to approximately 50 mL with CHCl₃. The polymer solution was precipitated into methanol and dried in vacuo at ambient temperature for 24 h and then at 100 °C overnight for ca. 16 h.
IIPU
Yield = 2.74 g, 84%. SEC analysis (CHCl$_3$ + 0.5% NEt$_3$) $M_w = 117.1$ kDa, $M_n = 14.4$ kDa, $M_p = 103.8$ kDa, $D_M = 8.12$. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 5.26 (t, $J = 6.0$ Hz, 2H), 5.12 (s, 2H), 4.60 (s, 2H), 4.19 (t, $J = 5.2$ Hz, 4H), 3.92 (q, $J = 5.6$ Hz, 4H), 2.78 (td, $J = 7.2$, 0.8 Hz, 4H). 2.63 (td, $J = 7.2$, 0.8 Hz, 4H), 2.57 – 2.46 (m, 4H), 1.61 – 1.53 (m, 4H), 1.44 – 1.25 (m, 8H).

IMPU
Yield = 3.07 g, 89%. SEC analysis (CHCl$_3$ + 0.5% NEt$_3$) $M_w = 95.6$ kDa, $M_n = 9.9$ kDa, $M_p = 87.1$ kDa, $D_M = 9.69$. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 5.34 (s, 2H), 5.09 (s, 2H), 4.77 – 4.57 (m, 2H), 4.28 – 4.12 (m, 4H), 4.06 (dd, $J = 9.1$, 6.6 Hz, 2H), 3.89 – 3.71 (m, 2H), 3.46 (p, $J = 5.4$ Hz, 4H), 2.77 (td, $J = 7.2$, 0.8 Hz, 4H), 2.62 (td, $J = 7.2$, 0.8 Hz, 4H), 2.57 – 2.48 (m, 4H), 1.63 – 1.51 (m, 5H), 1.44 – 1.24 (m, 8H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 172.04, 155.30, 85.47, 78.27, 72.73, 63.62, 40.27, 34.79, 32.23, 29.58, 29.18, 28.86, 27.11.

Physical blending procedure to make $bl$-II$_x$IM$_y$
IIPU and IMPU were combined in the indicated ratios (1.2 g polymer total: 0.6 g IIPU + 0.6 g IMPU; 0.3 g IIPU + 0.9 g IMPU; 0.9 g IIPU + 0.3 g IMPU) in a 20 mL scintillation vial and dissolved in 10 mL CHCl$_3$. After the polymers were fully solubilized, the solution was poured onto a teflon sheet (~10 × 10 cm) where it evaporated to dryness over several hours to afford a blended homopolymer sample. The materials were then further dried in vacuo at 100 °C overnight (ca. 16 h) to ensure complete solvent removal before heated compression molding.
NMR Spectra

Figure S2. $^1$H NMR spectrum of isomannide tosylate (400 MHz, 298 K, CDCl$_3$).

Figure S3. $^{13}$C NMR spectrum of isomannide tosylate (100.57 MHz, 298 K, CDCl$_3$).
**Figure S4.** $^1$H NMR spectrum of isoidide acetate (400 MHz, 298 K, CDCl$_3$).

**Figure S5.** $^{13}$C NMR spectrum of isoidide acetate (100.57 MHz, 298 K, CDCl$_3$).
Figure S6. $^1$H NMR spectrum of isoidide (400 MHz, 298 K, DMSO).

Figure S7. $^{13}$C NMR spectrum of isoidide (100.57 MHz, 298 K, DMSO).
**Figure S8.** $^1$H NMR spectrum of *isoidide urethane* (400 MHz, 298 K, CDCl$_3$).

**Figure S9.** $^{13}$C NMR spectrum of *isoidide urethane* (100.57 MHz, 298 K, CDCl$_3$).
Figure S10. $^1$H NMR spectrum of *isomannide urethane* (400 MHz, 298 K, CDCl$_3$).

Figure S11. $^{13}$C NMR spectrum of *isomannide urethane* (100.57 MHz, 298 K, CDCl$_3$).
Figure S12. $^1$H NMR spectrum of IIPU (400 MHz, 298 K, CDCl$_3$).

Figure S13. $^{13}$C NMR spectrum of IIPU (100.57 MHz, 298 K, CDCl$_3$).
Figure S14. $^1$H NMR spectrum of IMPU (400 MHz, 298 K, CDCl$_3$).

Figure S15. $^{13}$C NMR spectrum of IMPU (100.57 MHz, 298 K, CDCl$_3$).
Figure S16. $^1$H NMR spectrum of $co-II_{50}M_{50}$ (400 MHz, 298 K, CDCl$_3$).

Figure S17. $^{13}$C NMR spectrum of $co-II_{50}M_{50}$ (100.57 MHz, 298 K, CDCl$_3$).
Figure S18. $^1$H NMR spectrum of $\text{co-}{\text{II}}_{25}\text{dM}_{75}$ (400 MHz, 298 K, CDCl$_3$).

Figure S19. $^{13}$C NMR spectrum of $\text{co-}{\text{II}}_{25}\text{IM}_{75}$ (100.57 MHz, 298 K, CDCl$_3$).
Figure S20. $^1$H NMR spectrum of $\textit{co-II}75\text{IM}_25$ (400 MHz, 298 K, CDCl$_3$).

Figure S21. $^{13}$C NMR spectrum of $\textit{co-II}75\text{BM}_{25}$ (100.57 MHz, 298 K, CDCl$_3$).
Figure S22. $^1$H NMR spectrum of $bl-II_{50}IM_{50}$ (400 MHz, 298 K, CDCl$_3$).

Figure S23. $^1$H NMR spectrum of $bl-II_{25}IM_{75}$ (400 MHz, 298 K, CDCl$_3$).
Figure S24. $^1$H NMR spectrum of $bl$-$lI_{175}lM_{25}$ (400 MHz, 298 K, CDCl₃).
**SEC data of polymers**

**Figure S25.** Normalized size exclusion chromatograms of homopolymers and copolymers (CHCl₃, 0.5% NEt₃) analysis against poly(styrene) (PS) standards.

**Figure S26.** Mark-Houwink-Sakurada plots of intrinsic viscosity vs molar mass of homopolymers and copolymers (CHCl₃, 0.5% NEt₃). The α values were calculated from the gradient of the line and are consistent with a linear polymer in a good/theta solvent. (dashed: fitting line; solid: raw data).
Figure S27. Normalized size exclusion chromatograms of blended homopolymers and respective homopolymers (CHCl₃, 0.5% NEt₃) analysis against poly(styrene) (PS) standards. Note. The molecular weight distributions of the blended samples have a slightly different profile than those in Figure S25 since a different batch of IIPU and IMPU were used for blending. The SEC profiles of the IIPU and IMPU used to prepare the blends are shown above and values are shown in Table S3.
Thermogravimetric analysis of all polymer compositions

**Figure S28.** Thermogravimetric analysis of isomannide and isoidide polymers, copolymers and blends at a heating rate of 10 K·min⁻¹
Tensile curves of IIPU and IMPU

Figure S29. Stress vs strain curve for 3-day annealed polymer samples (a) IIPU (b) IMPU. $n = 5$

Comparison of IIPU and IMPU to Commercial polymers

Figure S30. Representative stress vs strain curves of IIPU, IMPU, High Density Polyethylene (HDPE), and Nylon-6 tested at 10 mm·min$^{-1}$ and 22 °C.
Elastic Recovery of IMPU

Figure S31. (a) Pictures illustrating the recovery of IMPU after deformation. (b) Bar chart summarizing the recovery of IMPU after tensile deformation analyzed using ImageJ software.
Impact of dispersity and molecular weight upon tensile properties

**Figure S32.** Stress vs strain curves for low $D_m$ and low $M_w$: a) IMPU and b) IIPU. c) Normalized size exclusion chromatograms of original homopolymers and the low $M_w$ and low $D_m$ homopolymers (CHCl$_3$, 0.5% NEt$_3$) analysis against poly(styrene) (PS) standards.
DSC thermograms of IIPU and IMPU

![DSC thermograms showing heating and cooling cycles of 3-day annealed polymers at a rate of 10 K·min⁻¹ (a) IIPU (b) IMPU.](image)

**Figure S33.** DSC thermograms showing heating and cooling cycles of 3-day annealed polymers at a rate of 10 K·min⁻¹ (a) IIPU (b) IMPU.

DSC thermograms of IIPU at different annealing temperatures

![DSC thermograms showing heating cycles of annealed IIPU (3 h at 25 or 50 °C) at a rate of 10 K·min⁻¹ after thermal history erased. ΔHₘ of as-pressed sample = 21.27 J·g⁻¹.](image)

**Figure S34.** DSC thermograms showing heating cycles of annealed IIPU (3 h at 25 or 50 °C) at a rate of 10 K·min⁻¹ after thermal history erased. ΔHₘ of as-pressed sample = 21.27 J·g⁻¹.
DSC thermograms of copolymers

Figure S35. DSC thermograms showing heating and cooling cycles of 3-day annealed copolymers at a rate of 10 K·min\(^{-1}\) (a) \textit{co-II} IM\(_{25}\) (b) \textit{co-II} IM\(_{50}\) (c) \textit{co-II} IM\(_{75}\).
DSC thermograms of physical blends

![DSC thermograms of physical blends](image)

**Figure S36.** DSC thermograms showing heating and cooling cycles of 3-day annealed copolymers at a rate of 10 K·min⁻¹ (a) **bl-II₇₅IM₂₅** (b) **bl-II₅₀IM₅₀** (c) **bl-II₂₅IM₇₅**.

DSC thermograms of commercial polymer samples

![DSC thermograms of commercial polymer samples](image)

**Figure S37.** DSC thermograms showing heating and cooling cycles of commercial polymer samples at a rate of 10 K·min⁻¹ (a) HDPE (b) Nylon-6.
Fitting of rheology data for entanglement molecular weight ($M_e$) calculation

Figure S38. (a) IIPU Storage and loss modulus plot of a frequency sweep between 140 °C and 170 °C (b) IMPU Storage and loss modulus plot of IIPU film between 100 °C and 130 °C (c) IIPU Time-temperature superposition (TTS) created from shifting data to 130 °C using WLF superposition. (d) IMPU Time-temperature superposition (TTS) created from shifting data to 130 °C using WLF superposition. TTS was fitted using the polydisperse double reptation theory in the REPTATE software package.
Simulation details of polymer model

**Figure S39.** Partial charge distribution on a polymer repeat unit (IIPU shown).

Molecular dynamic simulations

**Figure S40.** (a) Bulk simulation of IIPU. (b and c) Local conformation differences of IIPU (b) and IMPU (c) as a direct result of the isohexide center. (d) Hydrogen bonding formed in the IIPU chain.
$^1$H NMR stack of copolymers

Figure S41. $^1$H-NMR spectra of copolymers stacked to illustrate retention of feed ratio stereoisomers. The splitting of the highlighted peaks in the isommanide is a result of the chiral center adjacent to the -O-CH$_2$-, while the splitting is less pronounced in the isoidide unit.
Tensile curves of copolymers

Figure S42. Stress vs strain curves for 3-day annealed polymer samples (a) co-II\textsubscript{75}IM\textsubscript{25} (b) co-II\textsubscript{50}M\textsubscript{50} (c) co-II\textsubscript{25}IM\textsubscript{75}. \(n = 5\)

Thermomechanical comparison of copolymers

Figure S43. Representative tensile curves of isoidide and isomannide homopolymers and copolymers at 10 mm-min\(^{-1}\) strain rate (left). Initial heating run of 3-day annealed isoidide and isomannide homopolymers and copolymers at a 10 K-min\(^{-1}\) heating rate (right).
**Tensile curves of physical blends**

![Tensile curves of physical blends](image)

**Figure S44.** Stress vs strain curves for 3-day annealed polymer samples (a) *bl*-II75IM25 (b) *bl*-II50IM80 (c) *bl*-II25IM75. *n* = 4

**Thermomechanical comparison of physical blends**

![Thermomechanical comparison of physical blends](image)

**Figure S45.** Representative tensile curves of isoidide and isomannide homopolymers and physical blends at 10 mm·min⁻¹ strain rate (left). Initial heating run of 3-day annealed isoidide and isomannide homopolymers and physical blends at a 10 K·min⁻¹ heating rate (right).
Tensile curves of commercial polymers

Figure S46. Stress vs strain curves for commercial polymer samples (a) HDPE (b) Nylon-6.
**Bulk system molecular dynamics simulations**

**Copolymers**
- \textbf{co-II}_{25}\text{IM}_{50}: 1.27849 Å\(^{-1}\)
- \textbf{co-II}_{50}\text{IM}_{50}: 1.43989 Å\(^{-1}\)
- \textbf{co-II}_{75}\text{IM}_{25}: 1.05191 Å\(^{-1}\)

**Blends**
- \textbf{bl-II}_{25}\text{IM}_{50}: 0.7349 Å\(^{-1}\)
- \textbf{bl-II}_{50}\text{IM}_{50}: 0.92927 Å\(^{-1}\)
- \textbf{bl-II}_{75}\text{IM}_{25}: 0.72379 Å\(^{-1}\)

**Figure S47.** Molecular dynamics bulk simulations of isoidide and isomannide copolymers and physical blends. Calculated interfacial surface area displayed.
AFM of surface morphology for the blended and copolymers

**Figure S48.** Adhesion, height and slope (or hardness) AFM images of $co$-$II_{50} IM_{50}$ and $bl$-$II_{50} IM_{50}$. Observed heterogeneity of the adhesion in the blended sample indicates a phase separation and is further supported in the heterogeneity in the slope (or hardness). In contrast the copolymer displays more homogeneity in the adhesion and slope image, which suggest the copolymer is significantly more homogenous than the blended sample.
Contact angle of water-polymer interface

![Contact angle images](image)

**Figure S49.** Representative contact angle image of each sample: IIPU, IMPU, *bl*-II₅₀IM₅₀, *co*-II₅₀IM₅₀.

**Table S1.** Contact angle data for each sample: IIPU, IMPU, *bl*-II₅₀IM₅₀, *co*-II₅₀IM₅₀.

| Polymer sample | Contact angle (°) |
|----------------|------------------|
| IIPU           | 52.8 ± 2.0       |
| *bl*-II₅₀IM₅₀ | 59.0 ± 1.4       |
| *co*-II₅₀IM₅₀ | 48.9 ± 1.8       |
| IMPU           | 44.8 ± 1.0       |

Stand deviation of the measurements taken as error. n = 5
Quantitative degradation calculations

**Figure S50.** Overview schematic that describes model used to predict relative degradation rate ($k_{rel}$) values.

![Schematic diagram](image)

**Figure S51.** The $k_{rel}$ vs physical parameters for IIPU, IMPU and their copolymers as compared to PLA and PCL.

**Table S2.** Summary of key data values from quantitative model.

| Polymer   | Hydrophobicity ($\log P/SA$) | $k_{rel}$ |
|-----------|------------------------------|-----------|
| PLA       | 0.0036                       | 0.0967    |
| IIPU      | 0.0059                       | 1.42      |
| PCL       | 0.0096                       | 1.7       |
| co-II$_{25}$IM$_{25}$ | 0.0059   | 1.8       |
| co-II$_{50}$IM$_{50}$ | 0.0059   | 2.48      |
| IMPU      | 0.0059                       | 10.71     |
Table S3. Summary data table for thermomechanical properties of all polymers.

|          | \(M_w\) (kDa) | \(D_M\) | \(T_g^a\) (°C) | \(T_m^b\) (°C) | \(\Delta H_m^c\) (J·g\(^{-1}\)) | \(T_{d,5\%}^d\) (°C) | \(E^e\) (MPa) | \(\sigma_b^f\) (MPa) | \(\sigma_y^g\) (MPa) | \(\varepsilon_b^h\) (%) | \(U_T^i\) (MJ·m\(^{-3}\)) |
|----------|---------------|---------|--------------|---------------|-------------------------------|----------------------|------------|----------------|----------------|----------------|----------------|----------------|
| IIPU     | 117           | 8.12    | 15           | 111-158       | 23.9                          | 286                  | 320±66     | 56±5           | 16±1           | 989±114         | 329±63         |
| IMPU     | 95            | 9.69    | 15           | -             | -                             | 266                  | 3.7±0.3    | 39±5           | -              | 1285±68         | 187±18         |
| co-II\(_{75}\)IM\(_{25}\) | 81           | 9.95    | 18           | 40-92, 96-134 | 15.1                          | 271                  | 134±5      | 40±3           | 9±1            | 1151±41         | 253±19         |
| co-II\(_{50}\)IM\(_{50}\) | 79           | 7.81    | 16           | -             | -                             | 276                  | 3.0±0.3    | 55±3           | -              | 1658±84         | 279±24         |
| co-II\(_{25}\)IM\(_{75}\) | 89           | 7.77    | 17           | -             | -                             | 276                  | 3.5±0.6    | 54±11          | -              | 1344±80         | 228±59         |
| bl-II\(_{75}\)IM\(_{25}\) | 106          | 4.78    | 17           | 91-111, 116-156 | 18.9                      | 276                  | 350±43     | 44±3           | 19±1           | 740±51          | 218±24         |
| bl-II\(_{50}\)IM\(_{50}\) | 85           | 4.82    | 18           | 94-110, 127-155 | 13.6                      | 269                  | 272±10     | 37±5           | 13±1           | 462±100         | 123±37         |
| bl-II\(_{25}\)IM\(_{75}\) | 72           | 4.09    | 19           | 92-110, 124-151 | 7.9                       | 258                  | 139±32     | 49±6           | 5±0.5          | 1357±131        | 372±70         |
| IIPU*    | 123           | 5.62    | -            | -             | -                             | -                    | -          | -              | -              | -              | -              |
| IMPU*    | 64            | 4.50    | -            | -             | -                             | -                    | -          | -              | -              | -              | -              |
| HDPE     | -             | -       | -            | 86-140        | 170.5                         | -                    | 599±46     | 28±2           | 24±1           | 1145±117        | 234±29         |
| Nylon-6  | -             | -       | -            | 60            | 164-232                       | 87.0                 | -          | 215±11         | 67±4           | 55±2           | 336±60         |
| IMPUǂ    | 40            | 2.96    | -            | -             | -                             | -                    | -          | -              | -              | 1285±46         | 211±18         |
| IIPUǂ    | 37            | 2.30    | -            | -             | -                             | 395±69               | 39±1       | 19±1           | 604±3          | 159±1          |

(a) The \(T_g\) was obtained from 2nd heating cycle from the derivative (b) The \(T_m\) was taken as a range during 1st heating cycle (c) Total enthalpy of melting (\(\Delta H_m\)) was calculated by integration of all endothermic transitions. (d) Young's modulus (e) Stress at break (f) Stress at yield (g) Strain at break (h) Tensile toughness n ≥ 4. Uncertainty presented as the standard deviation of n samples. *Polymers used for physical blending; ŧLow dispersity and low molecular weight samples
Table S4. Equilibrium system densities.

| Polymer System | Density (g cm\(^{-3}\)) |
|----------------|-------------------------|
| II\(_{100}\)    | 0.953                   |
| IM\(_{100}\)    | 0.968                   |
| bl-II\(_{25}\)IM\(_{75}\) | 0.964                   |
| bl-II\(_{50}\)IM\(_{50}\) | 0.955                   |
| bl-II\(_{75}\)IM\(_{25}\) | 0.954                   |
| co-II\(_{25}\)IM\(_{75}\) | 0.958                   |
| co-II\(_{50}\)IM\(_{50}\) | 0.958                   |
| co-II\(_{75}\)IM\(_{25}\) | 0.955                   |

Table S5. Summary of data used to calculated the specific interfacial surface area.

| Polymer System | L (Å) | \(\Lambda_{\text{interface}}\) (Å\(^2\)) | \(V_{\text{sample}}\) (Å\(^3\)) | Specific Interfacial Area (Å\(^{-1}\)) |
|----------------|-------|---------------------------------|-----------------|-------------------------------------|
| bl-II\(_{25}\)IM\(_{75}\) | 52.965 | 189960.6 | 148582.2 | 1.27849 |
| bl-II\(_{50}\)IM\(_{50}\) | 53.2169 | 217009.7 | 150712.3 | 1.43989 |
| bl-II\(_{75}\)IM\(_{25}\) | 53.4479 | 160608.8 | 152683.4 | 1.05191 |
| co-II\(_{25}\)IM\(_{75}\) | 51.7984 | 102135.7 | 138979 | 0.7349 |
| co-II\(_{50}\)IM\(_{50}\) | 53.2128 | 140019.6 | 150677.5 | 0.92927 |
| co-II\(_{75}\)IM\(_{25}\) | 53.6005 | 111460.2 | 153995 | 0.72379 |

Table S6. Interaction parameters of polymer repeat unit (names are consistent with GAFF).

| id | Atom Types | Mass (g/mol) | \(\varepsilon_{\text{LJ}}\) (kCal/mol) | \(\sigma_{\text{LJ}}\) (Å) | Description |
|----|------------|--------------|--------------------------------------|-----------------|-------------|
| 1  | C          | 12.0107      | 0.086                                | 3.39967 | \(sp^2\) C in Carboxyl group |
| 2  | C3         | 12.0107      | 0.1094                               | 3.39967 | \(sp^3\) C in Aliphatic chain |
| 3  | HC         | 1.00794      | 0.0157                               | 2.649533 | H bonded to \(sp^3\) C |
| 4  | HN         | 1.00794      | 0.0157                               | 1.069078 | H bonded to N |
| 5  | N          | 14.0067      | 0.17                                 | 3.249999 | \(sp^2\) N in amide groups |
| 6  | O          | 15.9994      | 0.21                                 | 2.959922 | O double bonded in Carboxyl group |
| 7  | OS         | 15.9994      | 0.17                                 | 3.000012 | O in ester/ether bond |
| 8  | SS         | 32.065       | 0.25                                 | 3.563595 | \(sp^3\) S in thio-ester and thio-ether |

| id | Bond Types | \(k_r\) (kCal/mol Å\(^2\)) | \(r_{\text{eq}}\) (Å) | Description |
|----|------------|-----------------------------|-----------------|-------------|
| 1  | C-C3       | 328.3                       | 1.508 | C-C bond between aliphatic C and carboxyl group |
| id | Angle Types       | \( k_0 \) (kCal/mol rad^2) | \( \theta_{eq} \) (degree) | Description                                      |
|----|-------------------|----------------------------|-----------------------------|--------------------------------------------------|
| 2  | C3-N              | 478.2                      | 1.345                       | N-C bond between aliphatic C to amino group N     |
| 3  | C-O               | 648                        | 1.214                       | O-C double bond in carboxyl group                 |
| 4  | C-OS              | 411.3                      | 1.343                       | O-C single bond in carboxyl group                 |
| 5  | C3-C3             | 303.1                      | 1.535                       | C-C bond between aliphatic C                      |
| 6  | C3-HC             | 337.3                      | 1.092                       | C-H bond in aliphatic C chain                    |
| 7  | C3-N              | 330.6                      | 1.46                        | C-N bond in amide group                           |
| 8  | C3-OS             | 301.5                      | 1.439                       | C-O bond in ester bond                            |
| 9  | C3-SS             | 225.8                      | 1.821                       | C-S bond in thio-ether bond                       |
| 10 | HN-N              | 410.2                      | 1.009                       | N-H bond in amide group                           |

| id | Proper Dihedral Types | \( k_d \) (kCal/mol) | d | n | Description |
|----|------------------------|---------------------|---|---|-------------|
| 1  | C-C3-C3               | 63.3                | 110.53 |   |             |
| 2  | C-C3-HC               | 47.2                | 109.68 |   |             |
| 3  | C-N-C3                | 63.9                | 121.35 |   |             |
| 4  | C-N-HN                | 49.2                | 118.46 |   |             |
| 5  | C-OS-C3               | 63.6                | 115.14 |   |             |
| 6  | C3-C-O                | 68                  | 123.11 |   |             |
| 7  | C3-C-OS               | 69.3                | 111.96 |   |             |
| 8  | C3-C3-C3              | 63.2                | 110.63 |   |             |
| 9  | C3-C3-HC              | 46.4                | 110.05 |   |             |
| 10 | C3-C3-N               | 65.9                | 112.13 |   |             |
| 11 | C3-C3-OS              | 67.8                | 108.42 |   |             |
| 12 | C3-C3-SS              | 61.1                | 112.69 |   |             |
| 13 | C3-N-HN               | 46                  | 116.78 |   |             |
| 14 | C3-OS-C3              | 62.1                | 113.41 |   |             |
| 15 | C3-SS-C3              | 60.6                | 99.92  |   |             |
| 16 | HC-C3-HC              | 39.4                | 108.35 |   |             |
| 17 | HC-C3-N               | 49.8                | 109.5  |   |             |
| 18 | HC-C3-OS              | 50.9                | 108.7  |   |             |
| 19 | HC-C3-SS              | 42.5                | 108.76 |   |             |
| 20 | N-C-O                 | 75.8                | 122.03 |   |             |
| 21 | N-C-OS                | 74.7                | 115.25 |   |             |
| 22 | O-C-OS                | 76.2                | 122.43 |   |             |
|   | Bond          | Energy      | Scale | Root | Tag |
|---|---------------|-------------|-------|------|-----|
| 1 | C-C3-C3-HC    | 0.155556    | 1     | 3    |     |
| 2 | C-C3-C3-S     | 0.155556    | 1     | 3    |     |
| 3 | C3-C3-OS-C3   | 2.7         | -1    | 2    |     |
| 4 | C3-C3-C3-C3   | 0.155556    | 1     | 3    |     |
| 5 | C3-C3-C3-C3   | 0.18        | 1     | 3    |     |
| 6 | C3-C3-C3-C3   | 0.25        | -1    | 2    |     |
| 7 | C3-C3-C3-C3   | 0.2         | -1    | 1    |     |
| 8 | C3-C3-C3-HC   | 0.155556    | 1     | 3    |     |
| 9 | C3-C3-C3-HC   | 0.16        | 1     | 3    |     |
|10 | C3-C3-C3-OS   | 0.155556    | 1     | 3    |     |
|11 | C3-C3-C3-S    | 0.155556    | 1     | 3    |     |
|12 | C3-C3-N-C     | 0           | 1     | 2    |     |
|13 | C3-C3-N-C     | 0.5         | -1    | 4    |     |
|14 | C3-C3-N-C     | 0.15        | -1    | 3    |     |
|15 | C3-C3-N-C     | 0.53        | 1     | 1    |     |
|16 | C3-C3-N-HN    | 0           | 1     | 2    |     |
|17 | C3-C3-OS-C    | 0.383333    | 1     | 3    |     |
|18 | C3-C3-OS-C    | 0.383       | 1     | 3    |     |
|19 | C3-C3-OS-C    | 0.8         | -1    | 1    |     |
|20 | C3-C3-OS-C3   | 0.383333    | 1     | 3    |     |
|21 | C3-C3-OS-C3   | 0.383       | 1     | 3    |     |
|22 | C3-C3-OS-C3   | 0.1         | -1    | 2    |     |
|23 | C3-C3-S-C3    | 0.333333    | 1     | 3    |     |
|24 | HC-C3-C3-HC   | 0.155556    | 1     | 3    |     |
|25 | HC-C3-C3-HC   | 0.15       | 1     | 3    |     |
|26 | HC-C3-C3-N    | 0.155556    | 1     | 3    |     |
|27 | HC-C3-C3-OS   | 0.155556    | 1     | 3    |     |
|28 | HC-C3-C3-OS   | 0.25       | 1     | 1    |     |
|29 | HC-C3-C3-S    | 0.155556    | 1     | 3    |     |
|30 | HC-C3-N-C     | 0           | 1     | 2    |     |
|31 | HC-C3-N-HN    | 0           | 1     | 2    |     |
|32 | HC-C3-OS-C    | 0.383333    | 1     | 3    |     |
|33 | HC-C3-OS-C3   | 0.383333    | 1     | 3    |     |
|34 | HC-C3-S-C3    | 0.333333    | 1     | 3    |     |
|35 | N-C-OS-C3     | 2.7         | -1    | 2    |     |
| id | Improper Dihedrals | $k_d$ (kCal/mol) | d | n | Description |
|----|-------------------|------------------|---|---|-------------|
| 1  | C3-N-HN           | 1.1              | -1| 2 |             |
| 2  | C3-O-C-OS         | 10.5             | -1| 2 |             |
| 3  | N-O-C-OS          | 10.5             | -1| 2 |             |
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