Supplementary Information

Supramolecular Engineering Polyesters: Endgroup Functionalization of Glycol Modified PET with Ureidopyrimidinone

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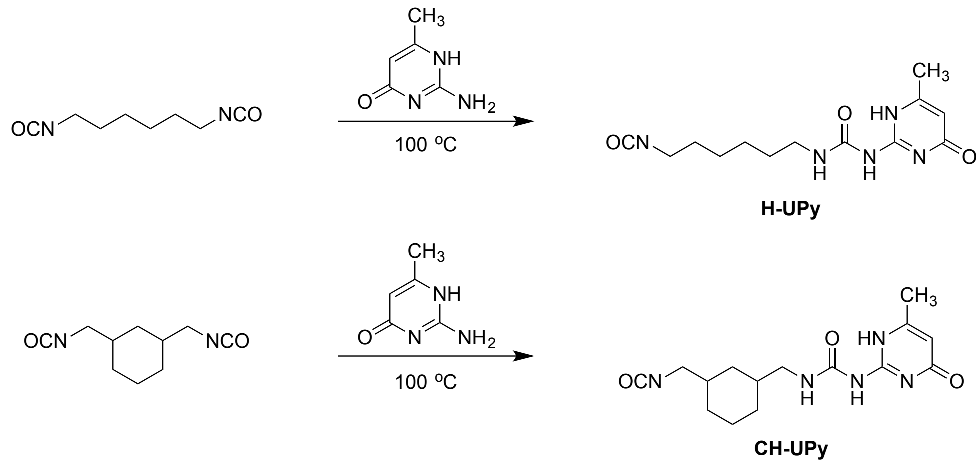
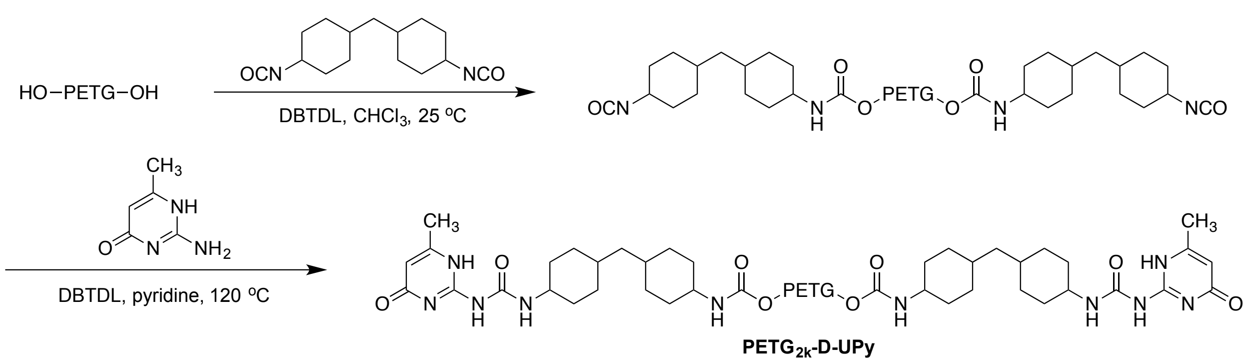
Table of Contents

Chemical Structures and Synthetic Schemes:



Scheme S1. Synthesis of endgroups H-UPy and CH-UPy



Scheme S2. One-pot synthesis of $PETG_{2k}$-D-UPy

Properties of PETG and H-UPy functionalized PETG of Higher Molecular Weights:

Table S1. Properties of PETG and H-UPy functionalized PETG of 3800 and 6800 g mol^{-1}.

Sample	$\langle M_n \rangle^a$ (g mol^{-1})	$\langle M_w \rangle^a$ (g mol^{-1})	Đ^a	5% Degradation^b (°C)	$T_g{}^c$ (°C)
$PETG_{3.8k}$	6100	10000	1.7	387	58
$PETG_{3.8k}$-H-UPy	10000	16000	1.6	360	71
$PETG_{6.8k}$	12000	21000	1.8	381	72
$PETG_{6.8k}$-H-UPy	17000	27000	1.6	371	72

^{a}Measured by GPC in $CHCl_3$ using polystyrene standards. ^{b}Measured by TGA. ^{c}Measured by DSC, mid-point of the second heat.

^{1}H NMR Spectra of Endgroups and Polymers:

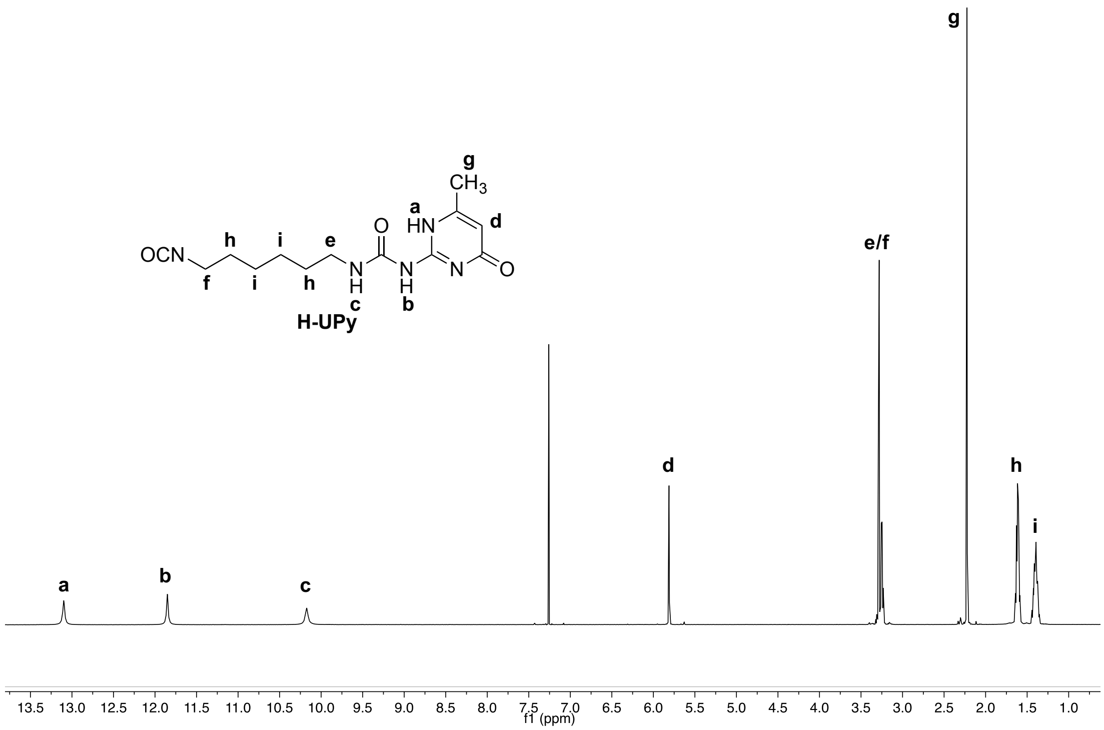


Figure S1. 1H NMR spectrum of H-UPy in CDCl3 at ambient temperature. 1H NMR (400 MHz, $CDCl_3$) δ: 13.10 (s, 1H), 11.85 (s, 1H), 10.18 (s, 1H), 5.81 (s, 1H), 3.28 (t, 2H), 3.25 (t, 2H), 2.22 (s, 3H), 1.61 (m, 4H), 1.40 (m, 4H).

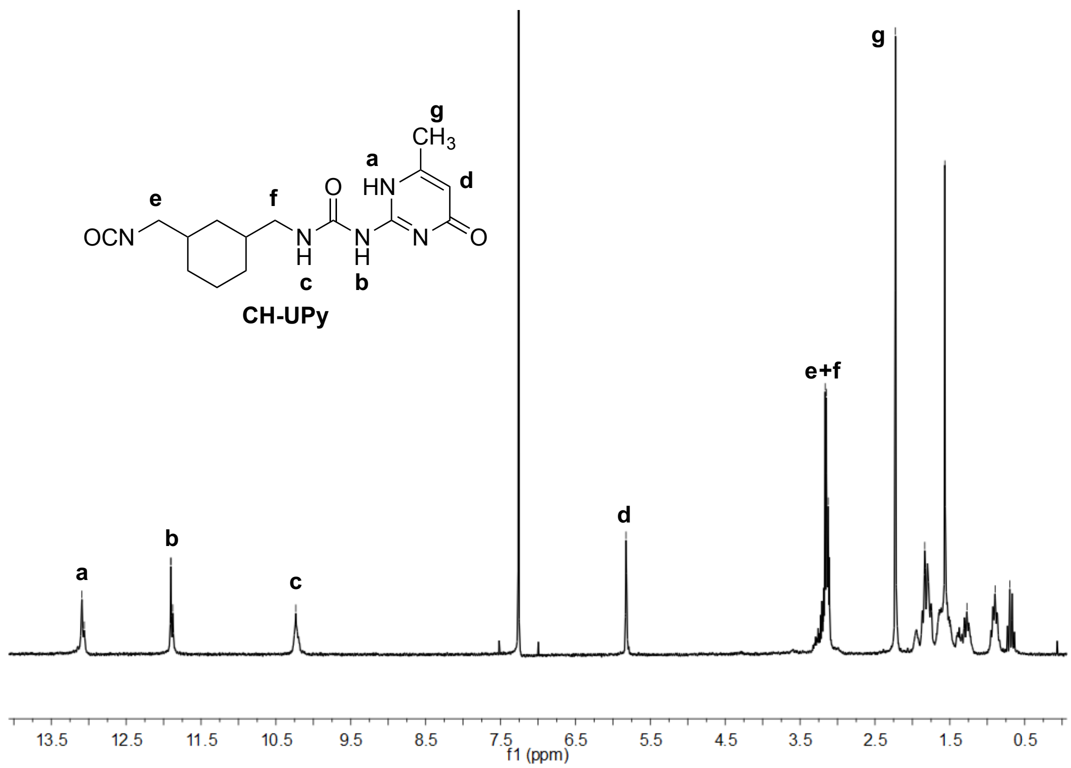


Figure S2. ^{1}H NMR spectrum of CH-UPy in $CDCl_3$ at ambient temperature.

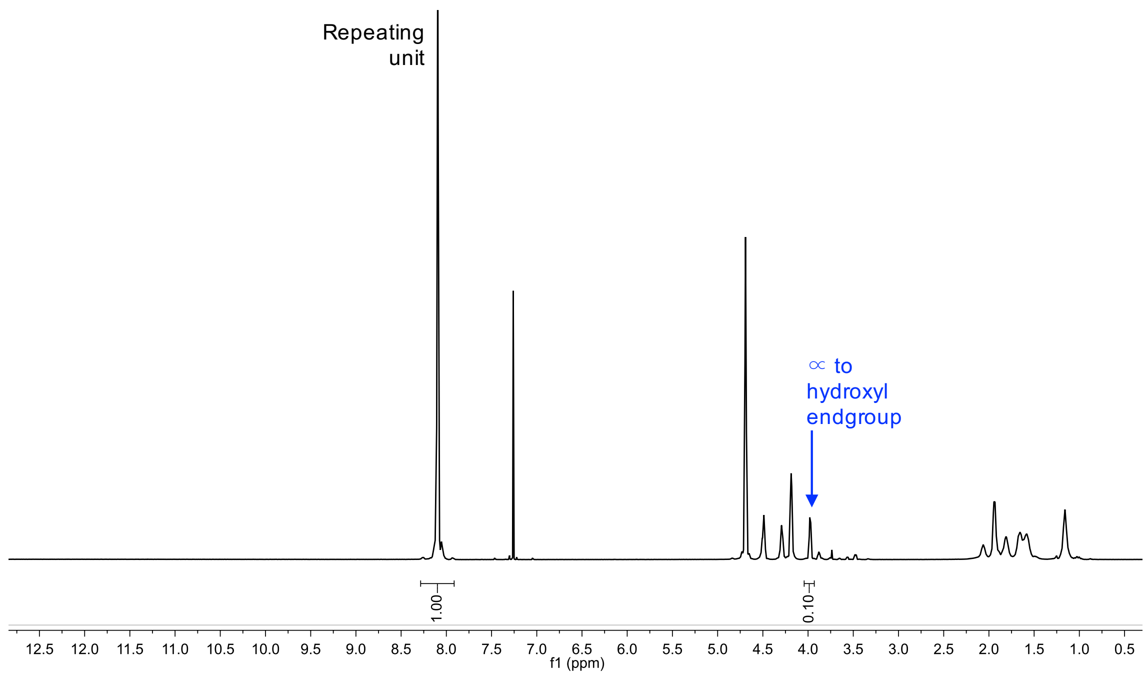


Figure S3. 1H NMR spectrum of PETG2k in CDCl3 at ambient temperature. The ratio of the integrals of the aromatic repeating unit (1.00) to the added integrals of the PETG peaks ∝ hydroxyl endgroups (0.10) was taken to find X_n.

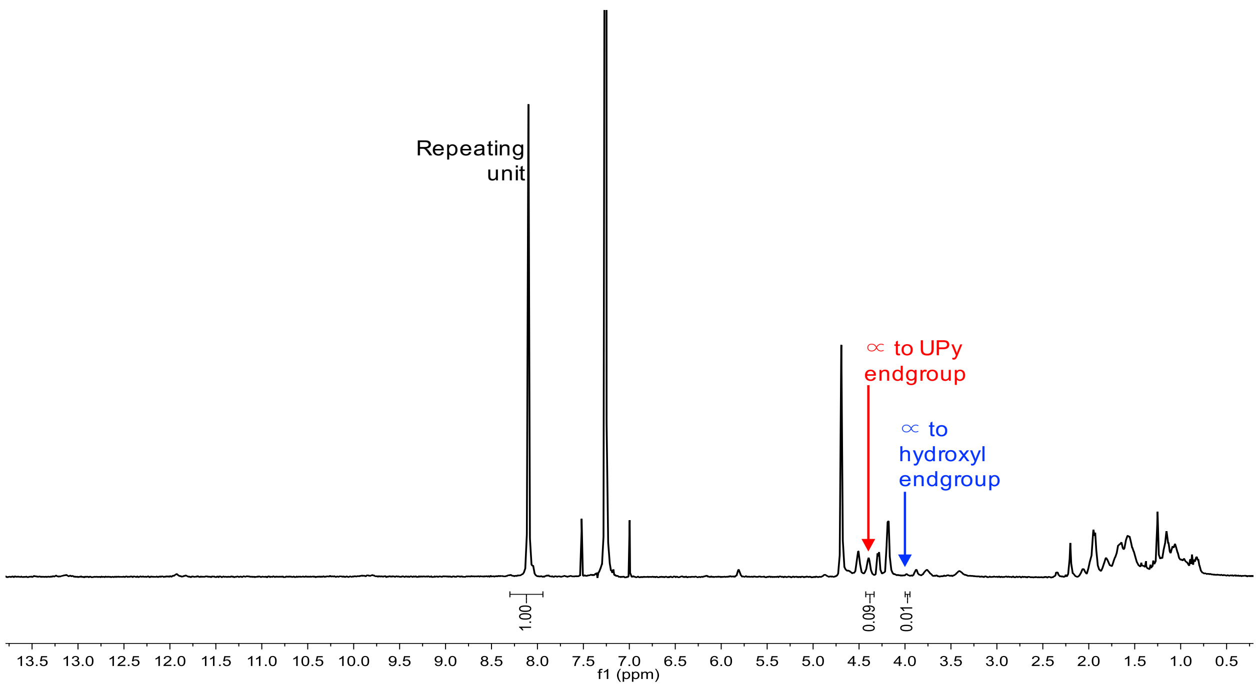


Figure S4. 1H NMR spectrum of PETG2k-D-UPy in CDCl3 at ambient temperature. The ratio of the integrals of the aromatic repeating unit (1.00) to the added integrals of the PETG peaks ∝ to the UPy endgroups and ∝ to existing hydroxyl endgroups (0.10) was taken to find X_n.

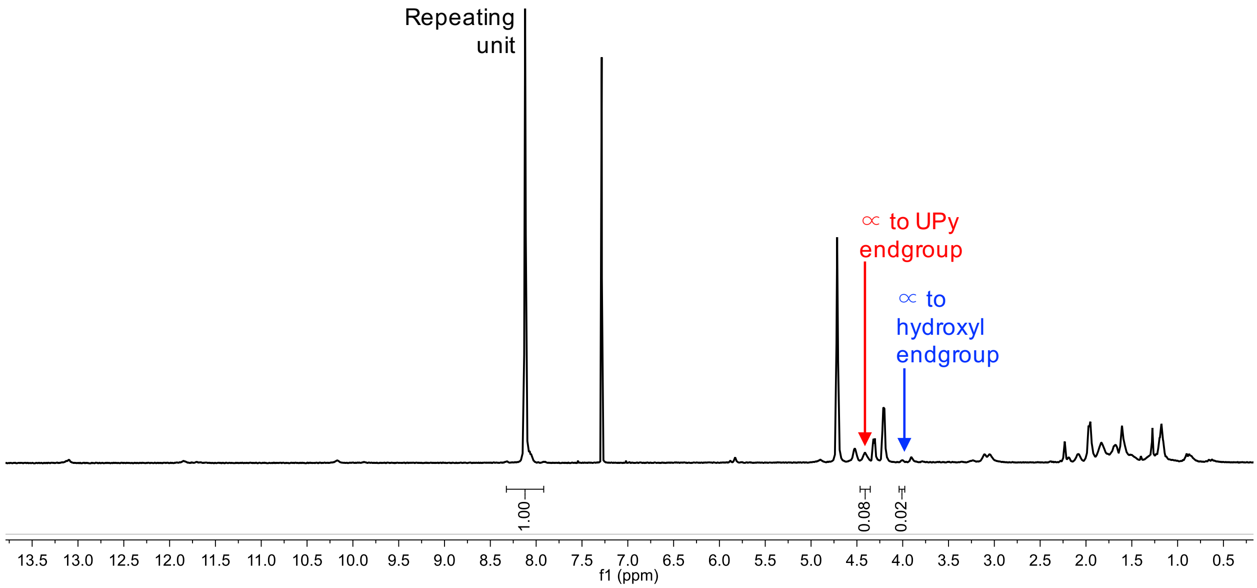


Figure S5. [1]H NMR spectrum of $PETG_{2k}$-CH-UPy in $CDCl_3$ at ambient temperature. The ratio of the integrals of the aromatic repeating unit (1.00) to the added integrals of the PETG peaks ∝ to the UPy endgroups and ∝ to existing hydroxyl endgroups (0.10) was taken to find X_n.

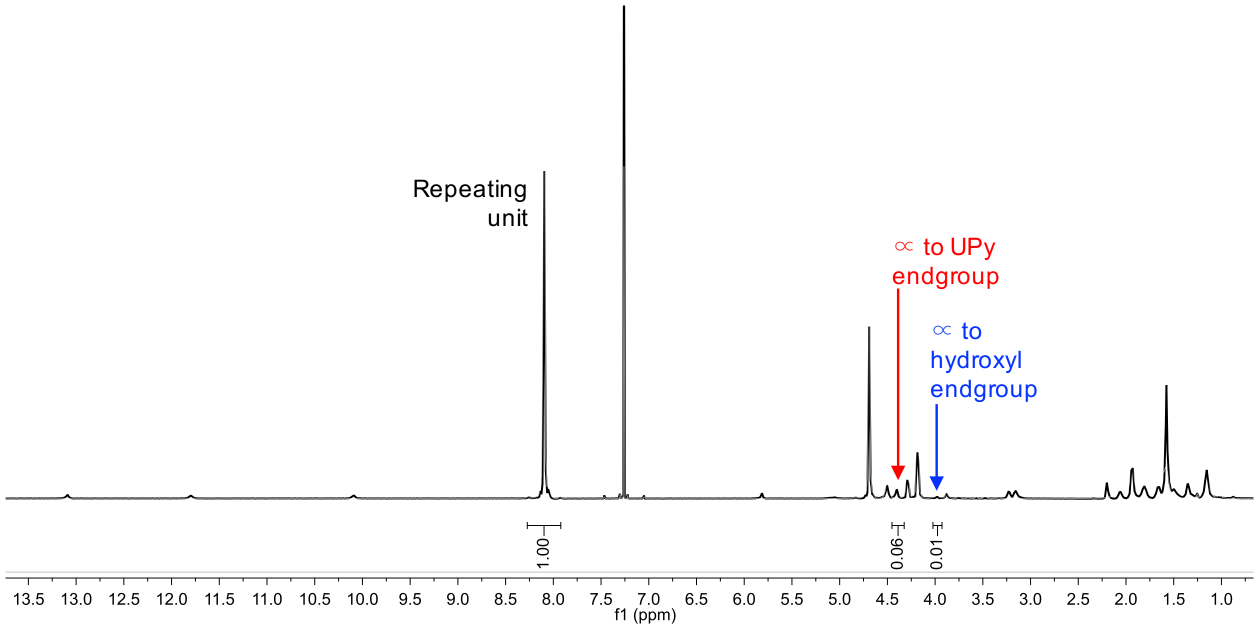


Figure S6. ^{1}H NMR spectrum of $PETG_{2k}$-H-UPy in $CDCl_3$ at ambient temperature. The ratio of the integrals of the aromatic repeating unit (1.00) to the added integrals of the PETG peaks ∝ to the UPy endgroups and ∝ to existing hydroxyl endgroups (0.07) was taken to find X_n.

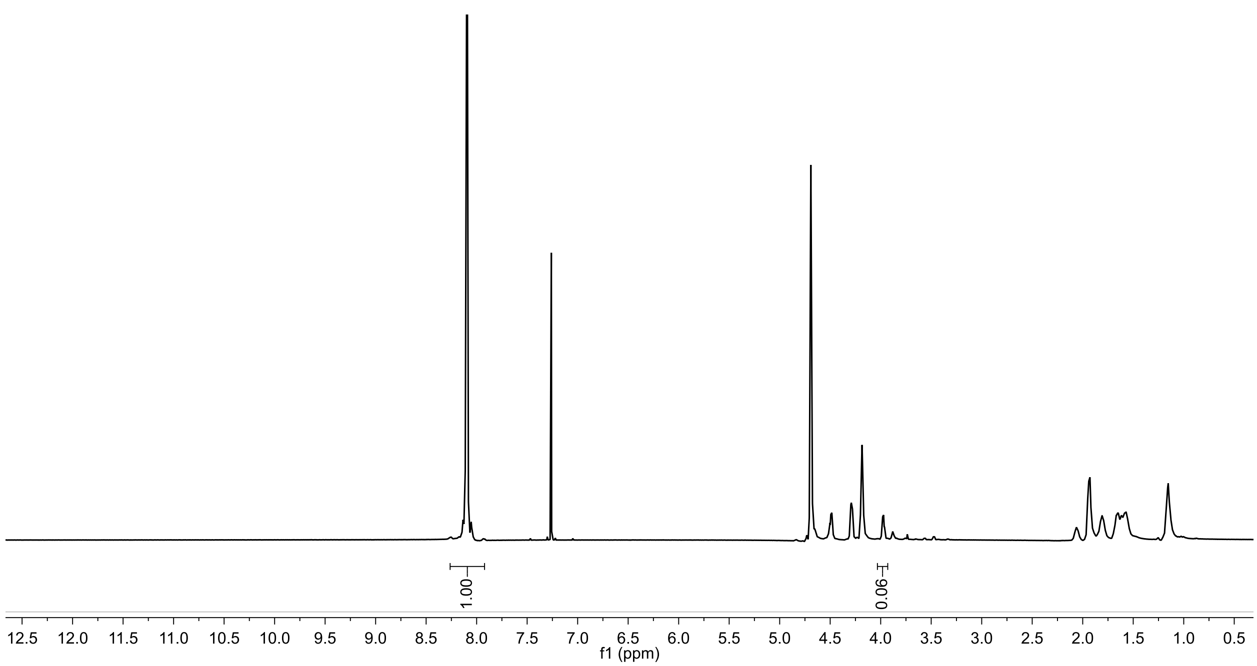


Figure S7. ^{1}H NMR spectrum of $PETG_{3.8k}$ in $CDCl_3$ at ambient temperature.

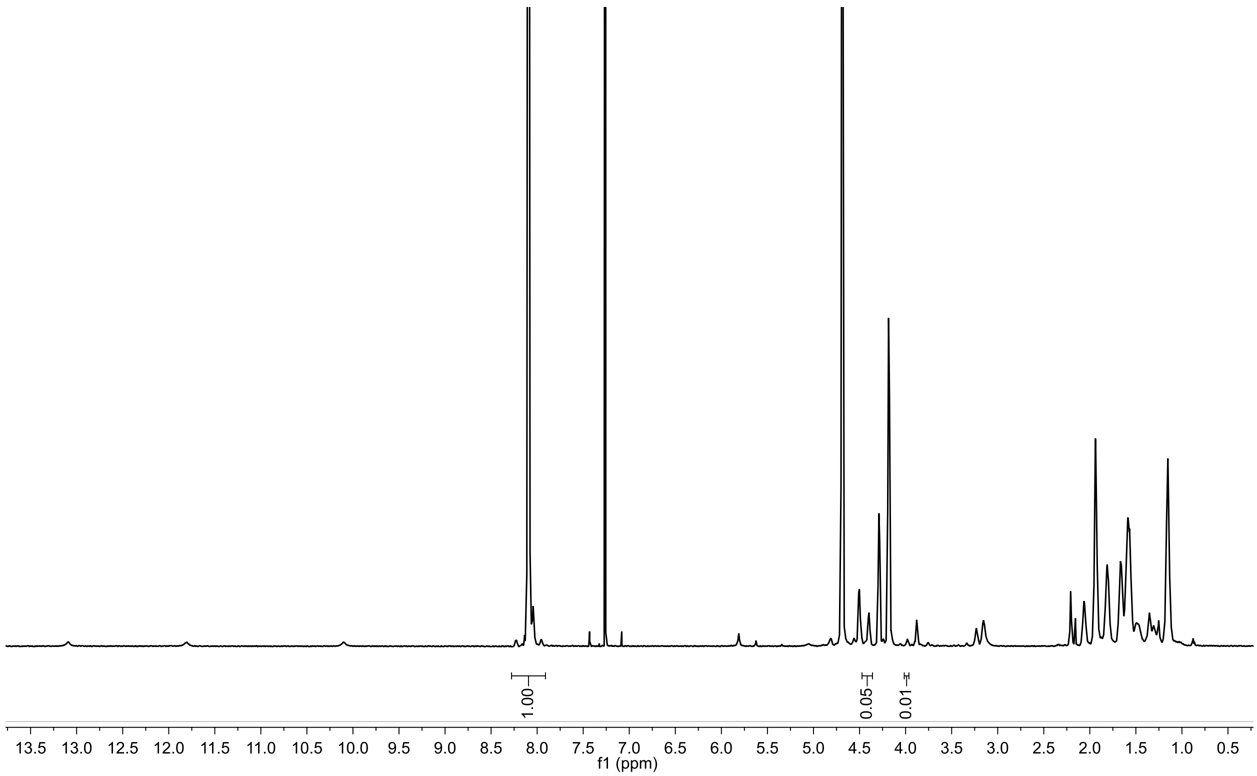


Figure S8. ^1H NMR spectrum of $PETG_{3.8k}$-H-UPy in $CDCl_3$ at ambient temperature.

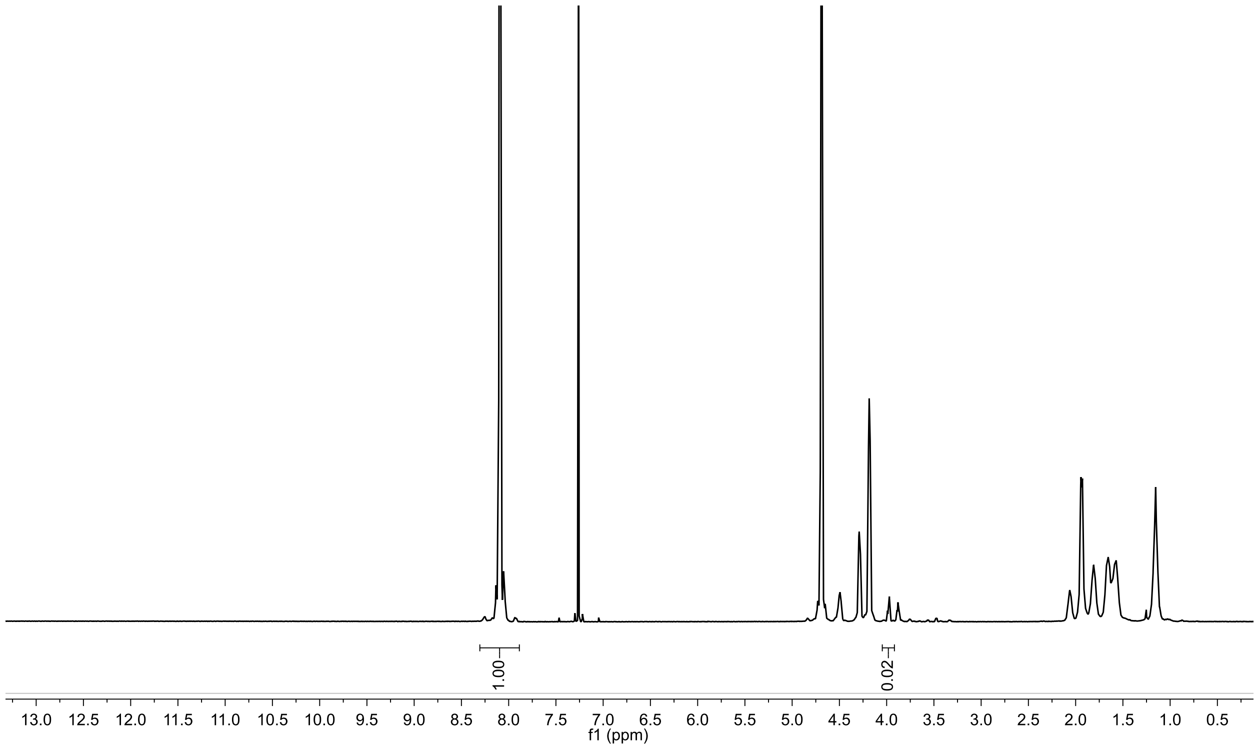


Figure S9. ^{1}H NMR spectrum of $PETG_{6.8k}$ in $CDCl_3$ at ambient temperature.

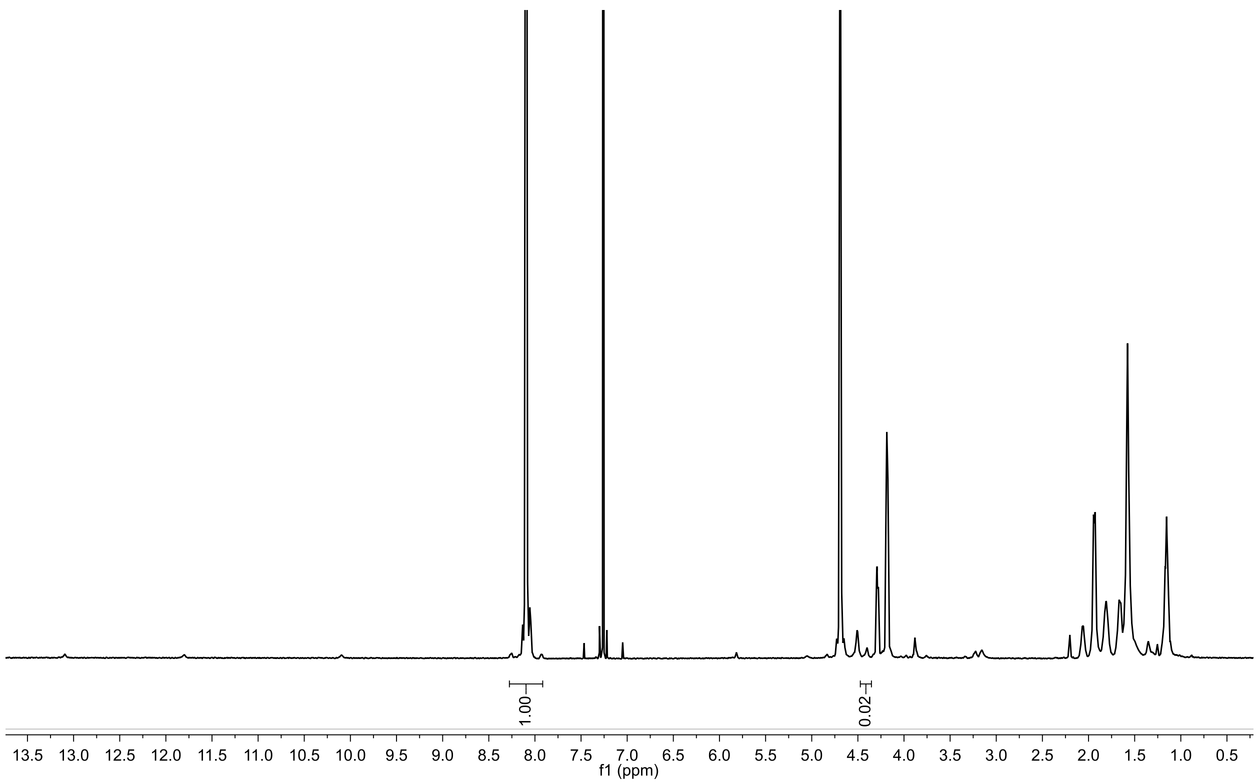


Figure S10. ^{1}H NMR spectrum of $PETG_{6.8k}$ in $CDCl_3$ at ambient temperature

ATR FT-IR Spectra:

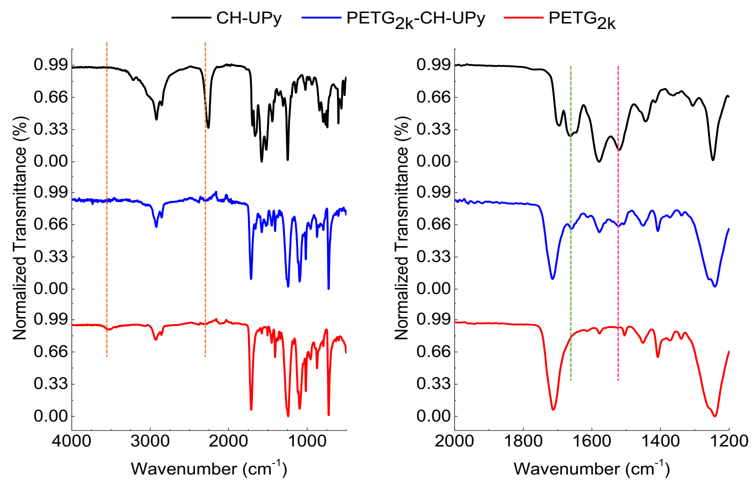


Figure S11. ATR FT-IR spectra of CH-UPy, PETG$_{2k}$-CH-UPy, and PETG$_{2k}$. The full spectra, on the left, depict the disappearance of the hydroxyl endgroup of PETG as well as the disappearance of the isocyanate functionality of CH-UPy.

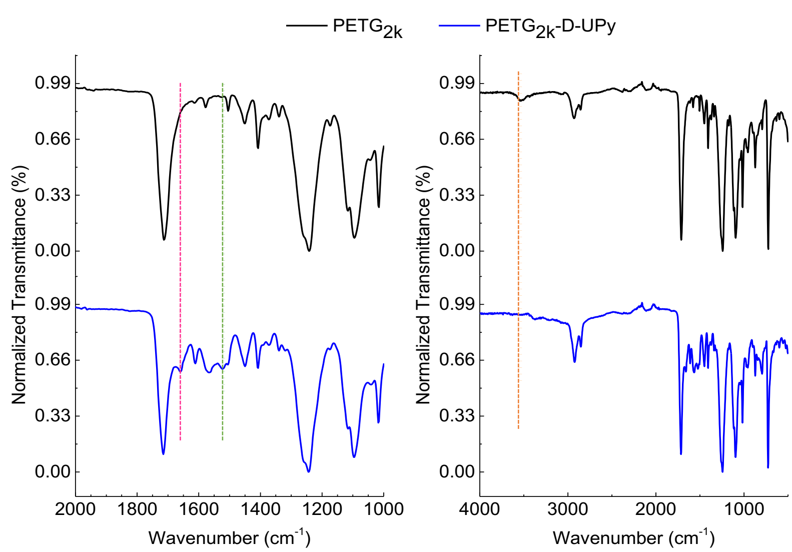


Figure S12. ATR FT-IR spectra of PETG$_{2k}$-D-UPy and PETG$_{2k}$. Peaks characteristic of the ureido endgroup are outlined in the spectra on the left. The full spectra, on the right, depict the disappearance of the hydroxyl endgroup of PETG.

TGA Curves:

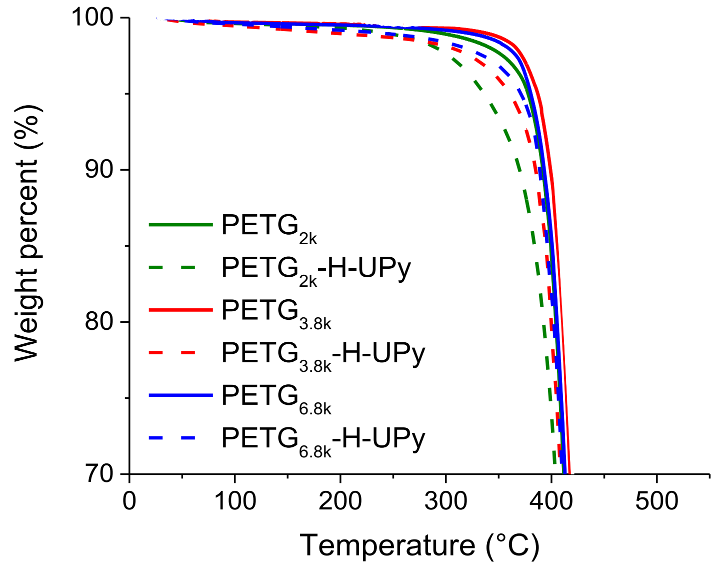


Figure S13. TGA Curves of all of the materials.

GPC Before and After Melt-Processing:

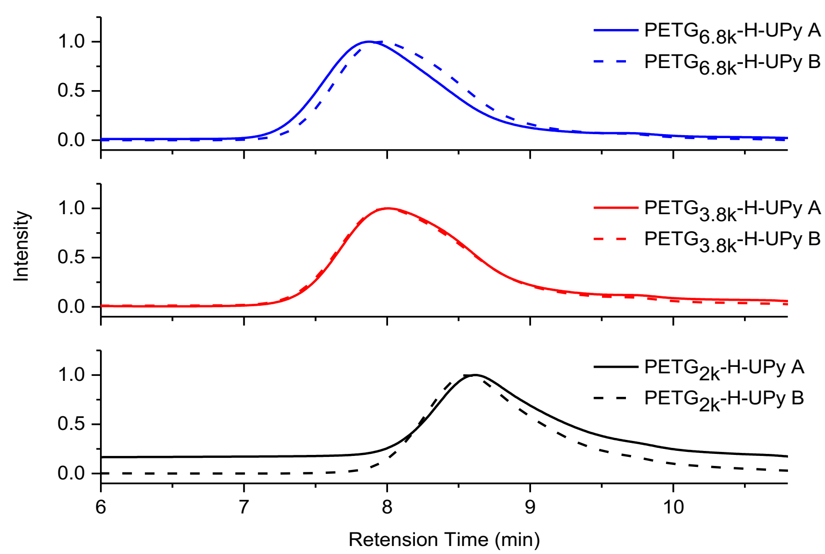


Figure S14. GPC traces A) of the raw powder run directly after synthesis, and B) of the melt-pressed materials ($CHCl_3$ at 25 °C and 1.0 mL min^{-1} using polystyrene standards).

Dynamic Oscillatory Shear Measurement of the Tan Delta:

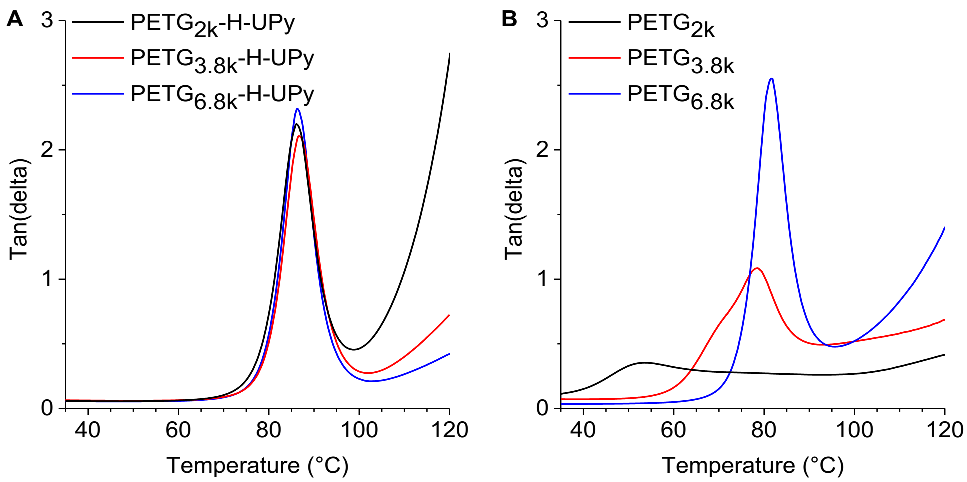


Figure S15. Dynamic oscillatory shear measurements of the tan delta as the material goes through cooling and heating cycles, where the peak signifies the T_g of A) H-UPy functionalized materials and B) unfunctionalized PETG (1 Hz, 0.1% strain, parallel plate fixture with plate diameter of 8 mm and gap length of 1000 μm).

AFM:

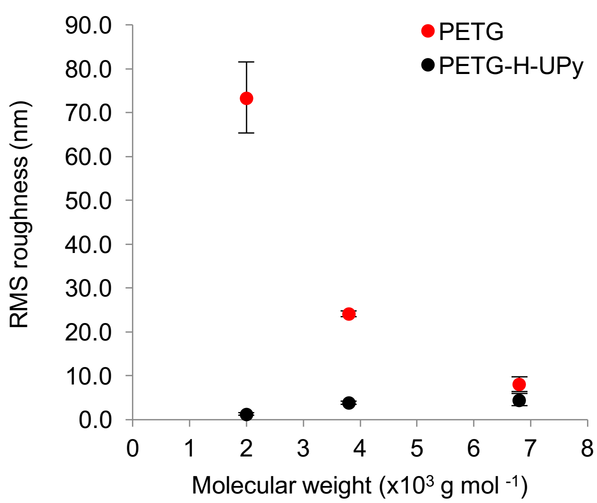


Figure S16. RMS surface roughness of PETG before and after H-UPy functionalization. RMS surface roughness obtained from AFM images (20x20 μm) using Nanoscope 6.14R1 software.

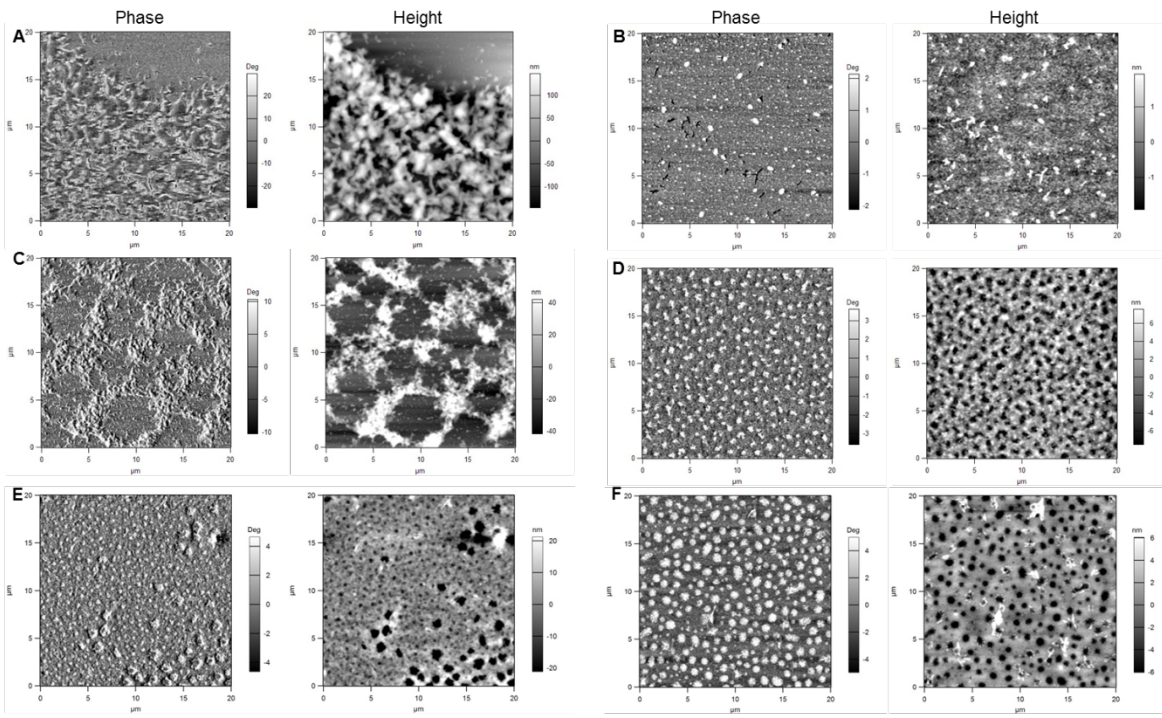


Figure S17. AFM 20x20 µm images: A) $PETG_{2k}$, B) $PETG_{2k}$-H-UPy, C) $PETG_{3.8k}$, D) $PETG_{3.8k}$-H-UPy, E) $PETG_{6.8k}$, F) $PETG_{6.8k}$-H-UPy.

Rheology:

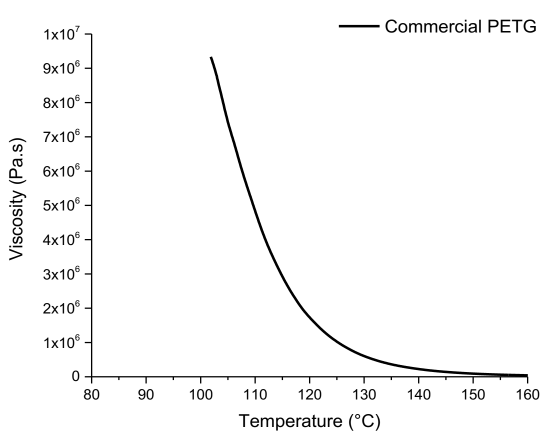


Figure S18. Rheological characterization of commercial PETG (shear rate 0.05 s^{-1}, parallel plate fixture with plate diameter of 8 mm and gap length of 1000 μm).

Variable Temperature ^{1}H NMR Spectra:

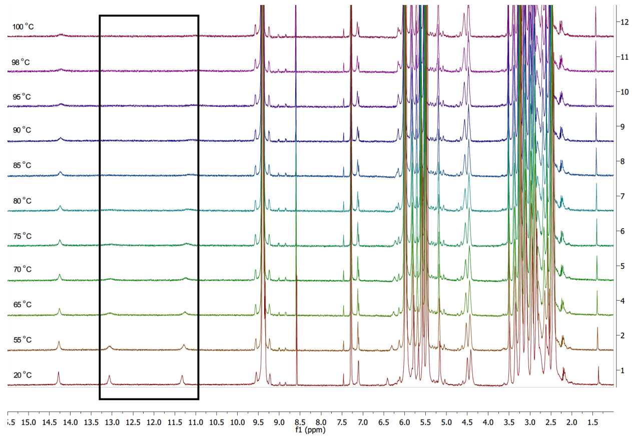


Figure S19. Variable temperature ^{1}H NMR spectra of PETG$_{6.8k}$-H-UPy in TCE-d$_2$ (c = 5 mM, 600 s equilibrium allowed at each temperature). The box outlines peaks that signify the presence of intermolecular H-bonding of UPy endgroups.