Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A one-pot, solvent-free, and controlled synthetic route for thermoresponsive hyperbranched polyurethanes

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Section I: Determination of the structural parameters of the precursors and HPUs

The absolute number average molar masses of PEG and PCL-triol were calculated using Equations S1a and S1b, respectively, in which A_{H_a} and A_{H_c} are the areas of the signals in the NMR spectrum assigned to H_a and H_c hydrogens of the monomeric unit and chain terminations of PEG (**Figure S1a**), while A_{H_d} and A_{H_e} are the areas of the signals of the H_d and H_e hydrogens of monomeric unit and chain terminations for PCL-triol (**Figure S1c**). The molar masses of PEG monomeric unit ($M_{u,\ PEG}$) and the monomer at the chain end are 44 and 45 g mol^{-1}, respectively, while for PCL-triol, the values are 114 and 115 g mol^{-1}, respectively.

$$M_{n,PEG} = \frac{44 \times \frac{A_{H_a}}{4} + (2 \times 45)}{\frac{A_{H_c}}{4}} \quad \textbf{(S1a)}$$

$$M_{n,\ PCL} = \frac{(114\ \times \frac{A_{H_d}}{2}) + (2 \times 115)}{\frac{A_{H_e}}{6}} \quad \textbf{(S1b)}$$

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The mass fractions of PEG (f_{PEG}), PCL-triol (f_{PCL}), and IPDI (f_{IPDI}) in the HPUs were calculated by Equations S2a, S2b, and S2c, respectively, using ^{1}H NMR data, where A_{H_a}, A_{H_e}, and A_{H_f} are the areas of the signals assigned to hydrogens of IPDI, PEG, and PCL-triol segments, respectively (**Figure S4a**), and M_u is the mass of the monomeric unit.

$$f_{PEG} = \frac{\frac{A_{H_a}}{4} \times M_{u,\,PEG}}{(\frac{A_{H_a}}{4} \times M_{u,\,PEG}) + (\frac{A_{H_p}}{2} \times M_{u,\,PCL}) + (\frac{A_{H_h}}{2} \times M_{u,\,IPDI})}$$

(S2a)

$$f_{PCL} = \frac{\frac{A_{H_p}}{2} \times M_{u,\,PCL}}{(\frac{A_{H_a}}{4} \times M_{u,\,PEG}) + (\frac{A_{H_p}}{2} \times M_{u,\,PCL}) + (\frac{A_{H_h}}{2} \times M_{u,\,IPDI})}$$

(S2b)

$$f_{IPDI} = \frac{\frac{A_{H_h}}{2} \times M_{u,\,IPDI}}{(\frac{A_{H_a}}{4} \times M_{u,\,PEG}) + (\frac{A_{H_p}}{2} \times M_{u,\,PCL}) + (\frac{A_{H_h}}{2} \times M_{u,\,IPDI})}.$$

(S2c)

The molar fractions (x_i) of the precursors into the polymer chains were calculated by the equations:

$$x_{PEG} = \frac{\frac{A_{H_a}}{4}}{(\frac{A_{H_a}}{4}) + (\frac{A_{H_p}}{2}) + (\frac{A_{H_h}}{2})}$$

(S3a)

$$x_{PCL} = \frac{\frac{A_{H_p}}{2}}{(\frac{A_{H_a}}{4}) + (\frac{A_{H_p}}{2}) + (\frac{A_{H_h}}{2})}$$

(S3b)

$$x_{IPDI} = \frac{\frac{A_{H_h}}{2}}{(\frac{A_{H_a}}{4}) + (\frac{A_{H_p}}{2}) + (\frac{A_{H_h}}{2})}.$$

(S3c)

Conversion (p) was calculated in terms of consumed hydroxyl groups derived from PEG. First, the initial molar ratio of the PEG monomers and hydroxyl groups was determined by ^{1}H NMR (spectrum shown in **Figure S1a**) to be 5.6. Afterwards, the conversion was calculated by Equation S4.

$$p = 1 - \left[\frac{5.6 \times \left(\frac{A_{H_c}}{2} \right)}{\frac{A_{H_a}}{4}} \right] \quad \textbf{(S4)}$$

The molar fraction of the HPU chain ends with hindered urea end-capped (x_{HU}) or hydroxyls group (x_{OH}) were estimated considering the differences between the IPDI molar fraction values for HPU and reaction medium as follows:

$$x_{HU} = 50 \times \left[\frac{(x_{IPDI})_{HPU}}{(x_{IPDI})_{reaction\ medium}} \right] \quad \textbf{(S5)}$$

$$x_{OH} = 100 - x_{HU} \quad \textbf{(S6)}$$

Section II: NMR spectra

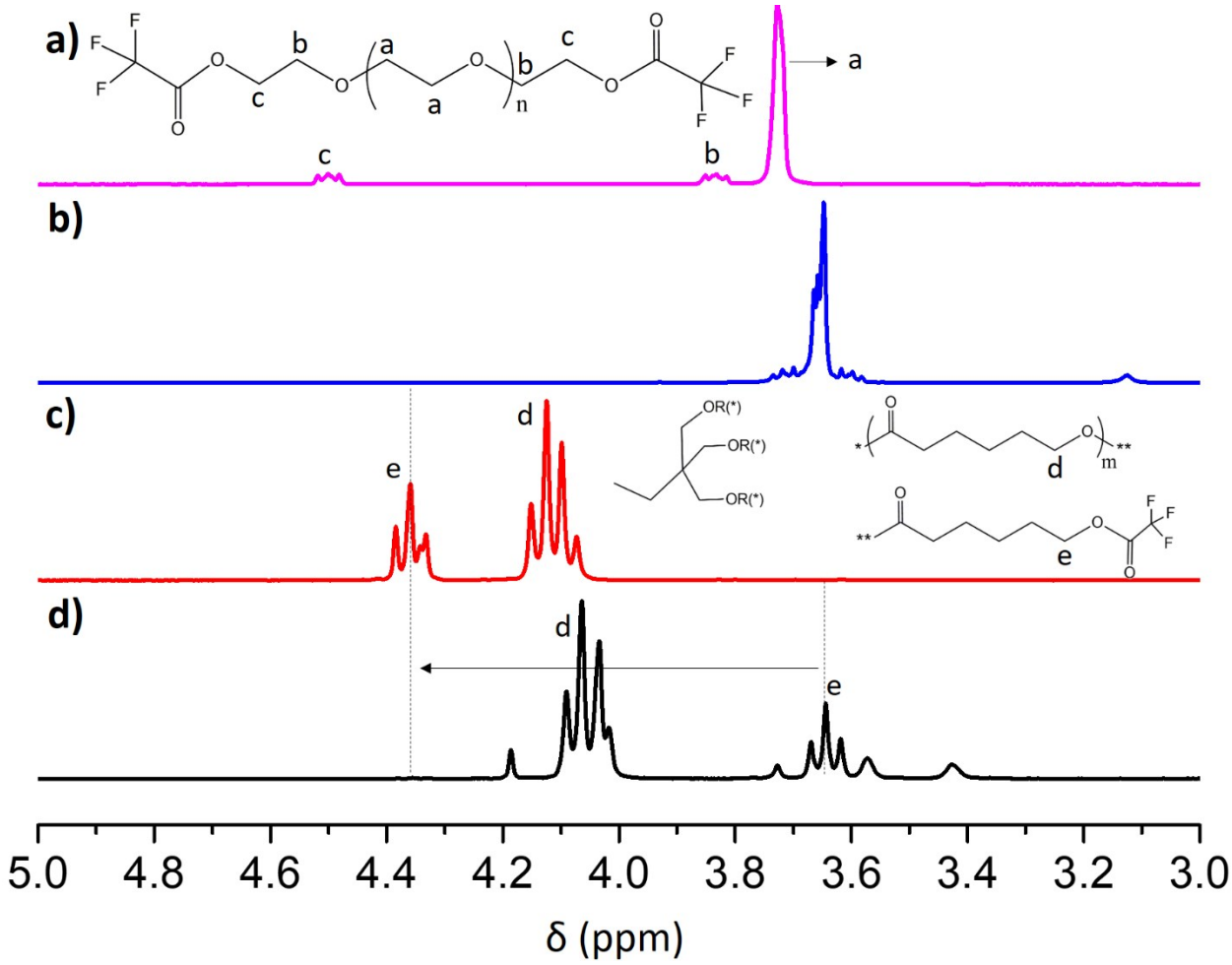


Figure S1. ^{1}H NMR spectra of a) acetylated PEG, b) PEG, c) acetylated PCL-triol, and d) PCL-triol.

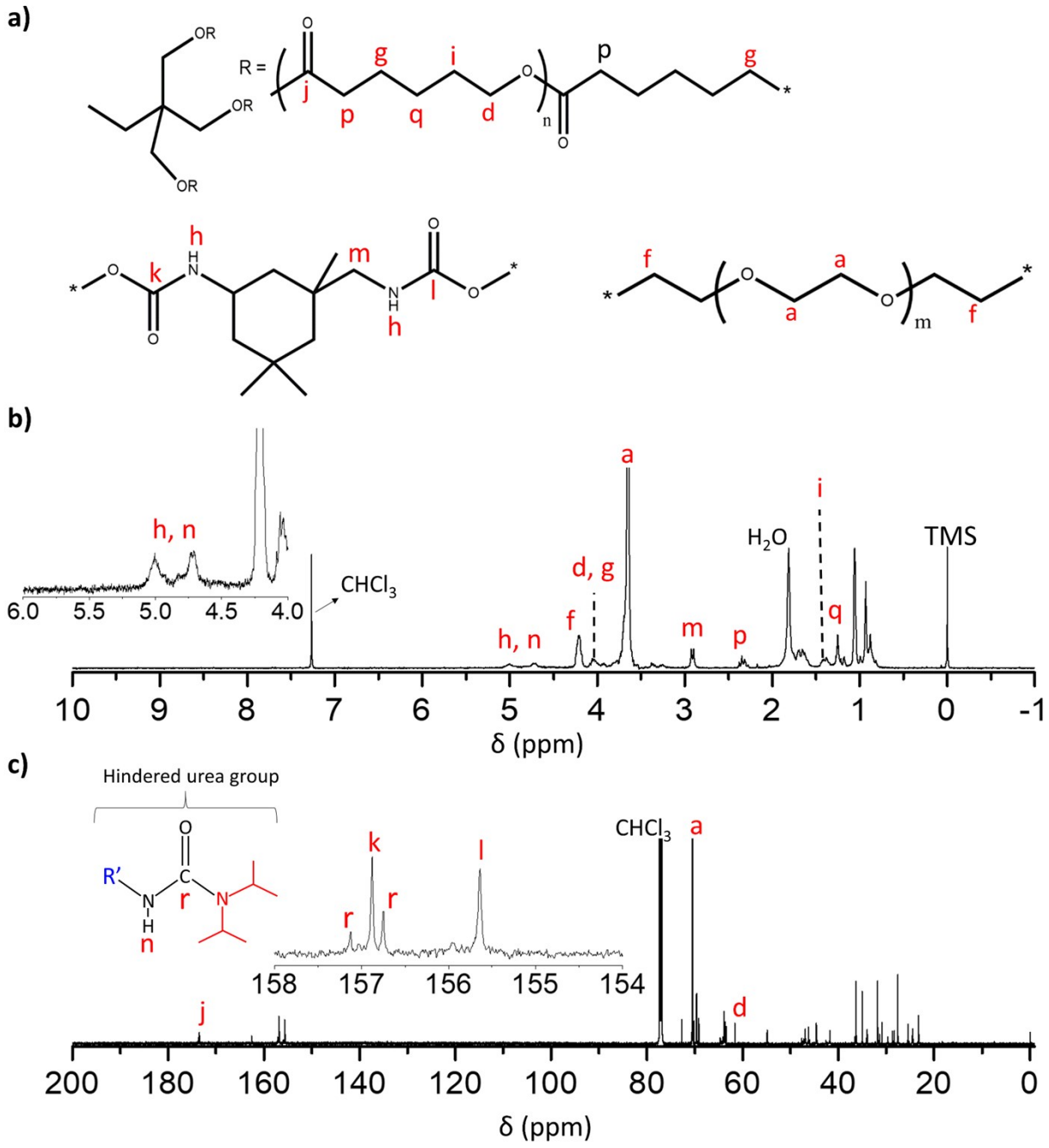


Figure S2. a) Chemical structure of HPU1, with labeled carbons and hydrogens, b) ^{1}H NMR and c) ^{13}C NMR spectra of HPU1. *Presence of a covalent bond between PEG or PCL-triol chain terminations and the oxygen from the urethane group; R' represents an IPDI chain termination of the HPU.

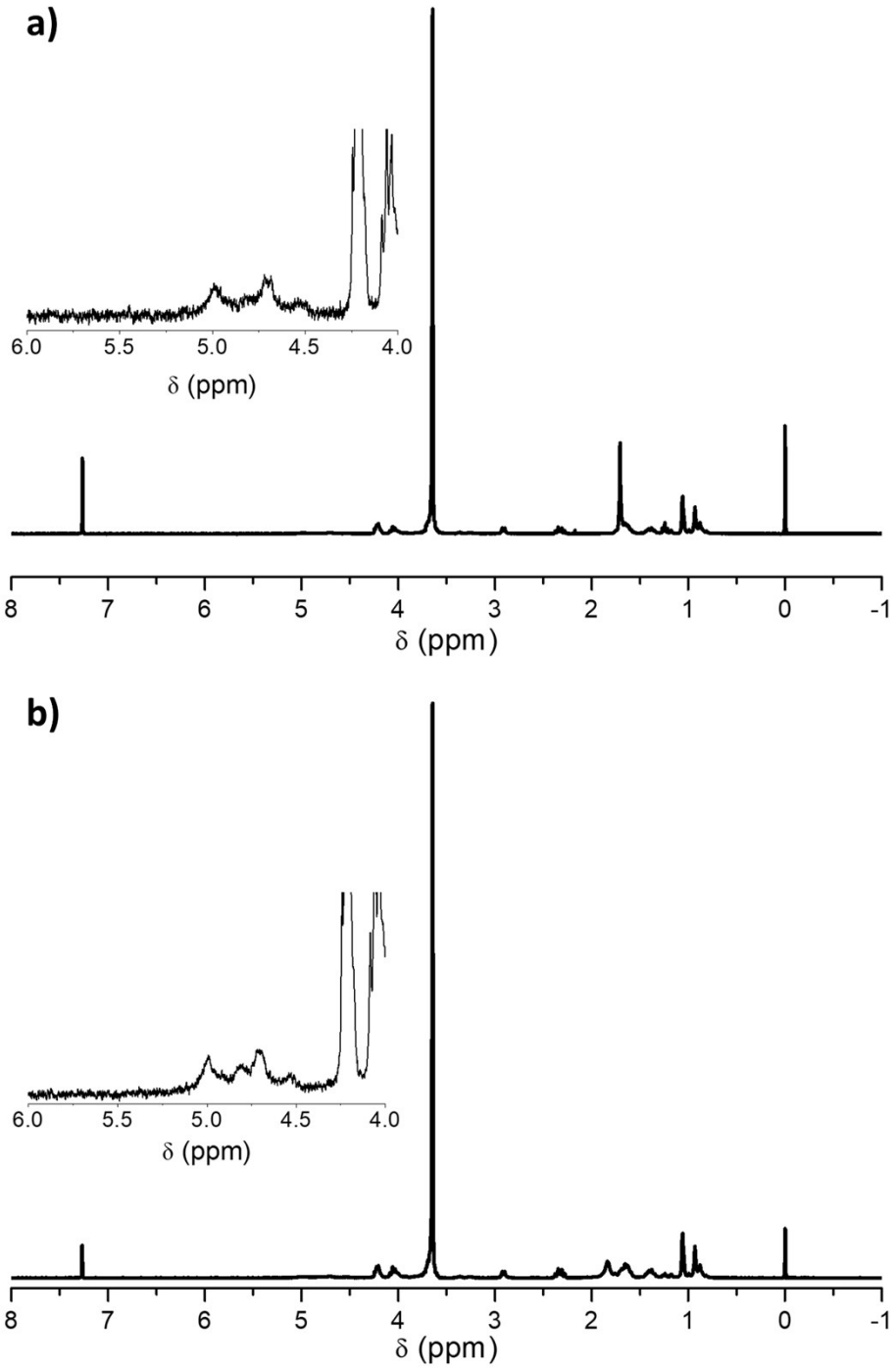


Figure S3. ^{1}H NMR spectra of a) HPU2 and b) HPU3.

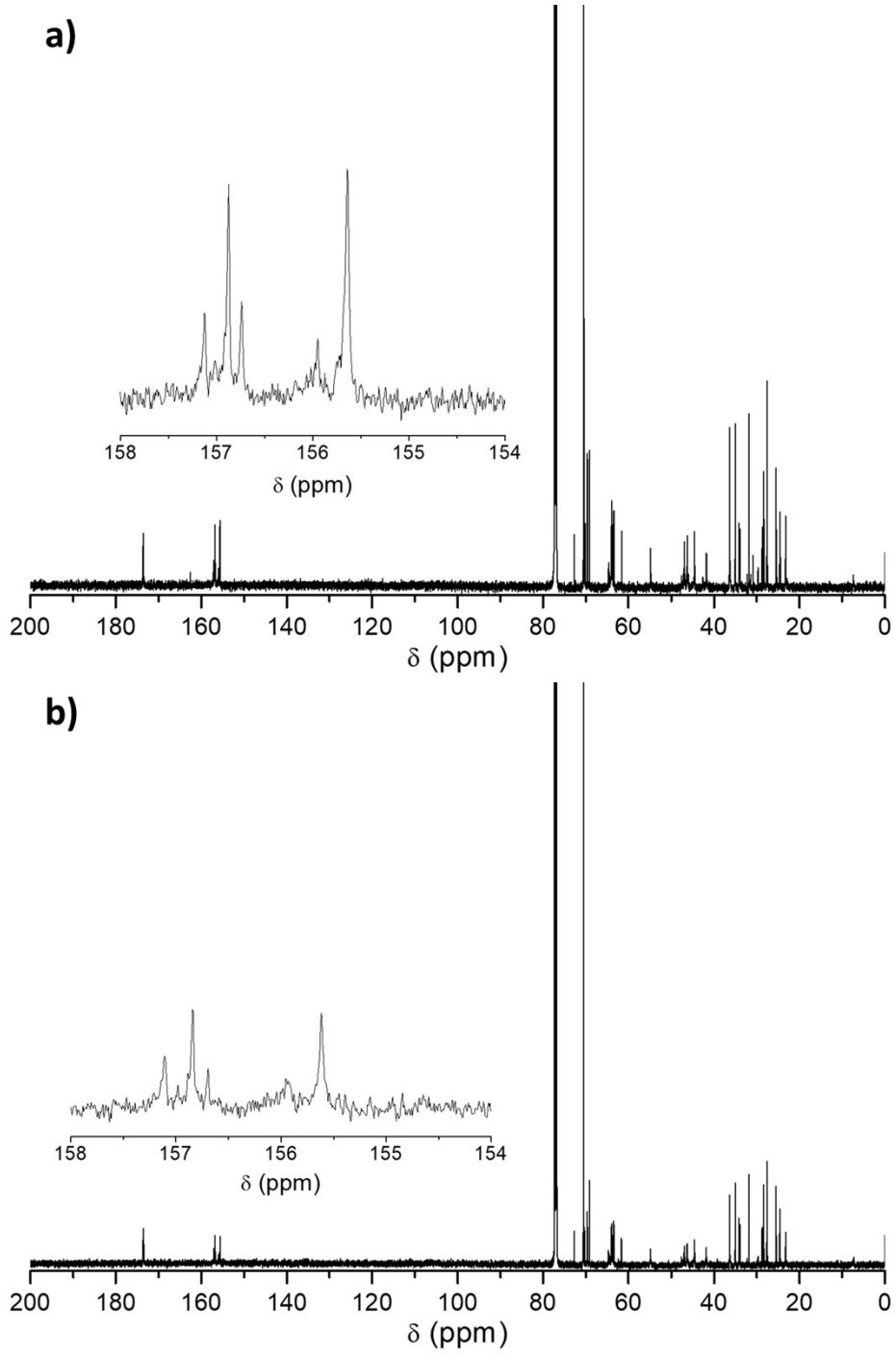
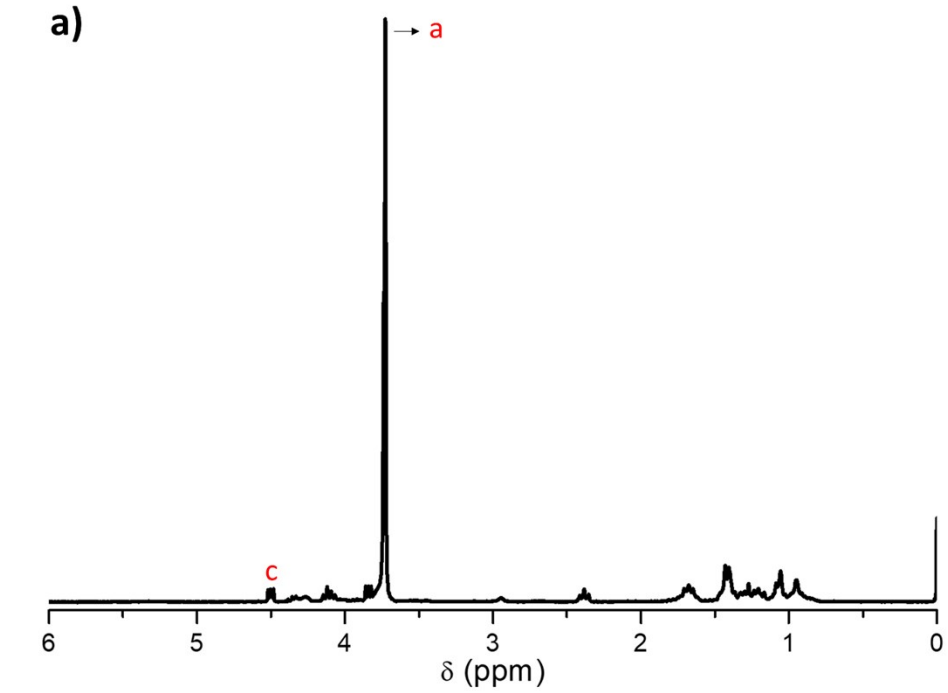


Figure S4. ^{13}C NMR spectra of a) HPU2 and b) HPU3.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c
6
5
4
3
2
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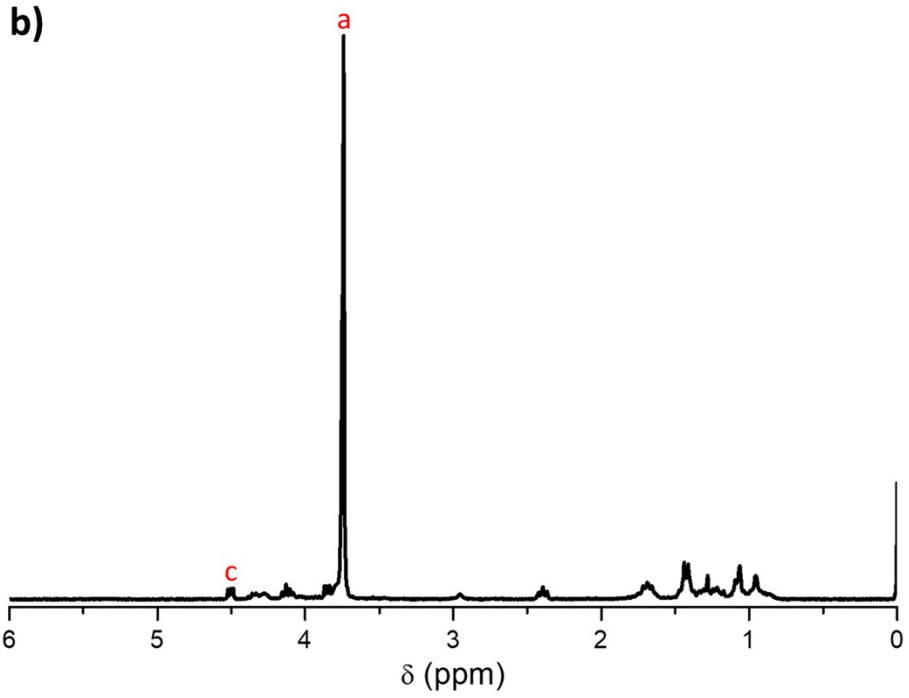
0
δ (ppm)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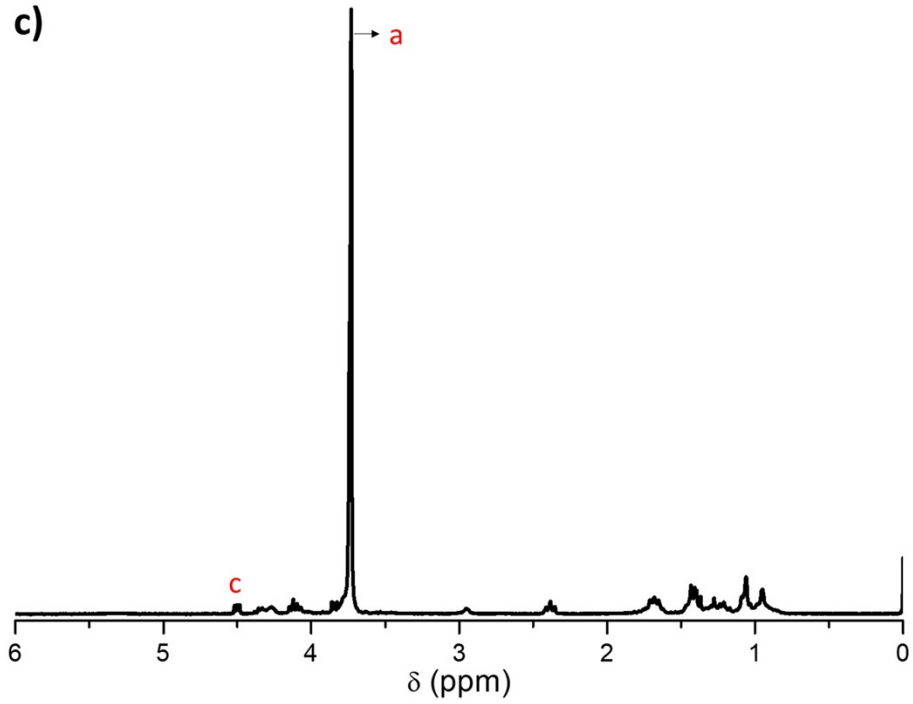
δ (ppm)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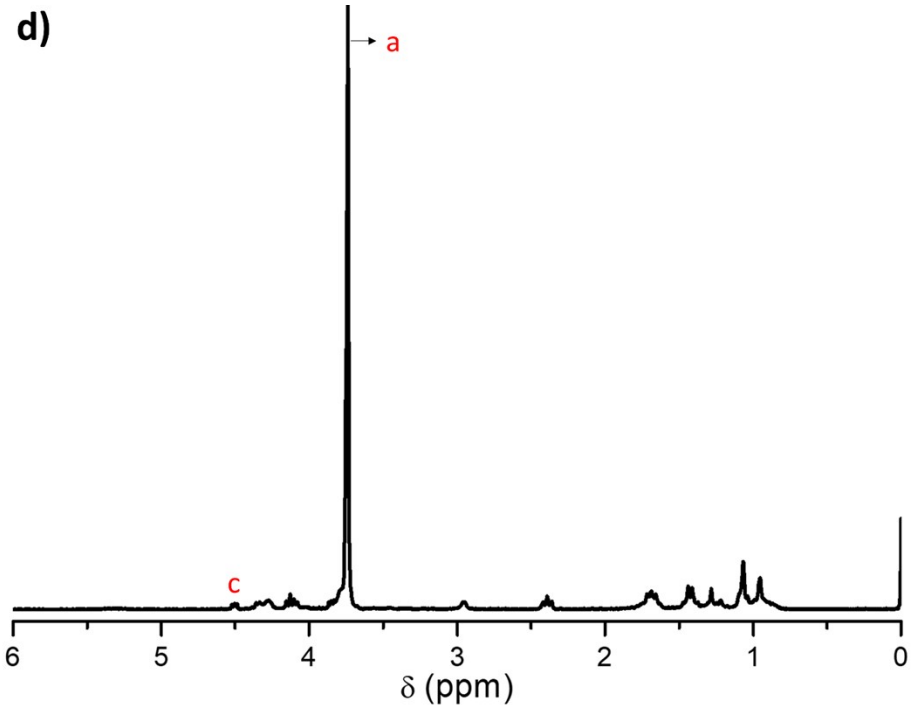
0
δ (ppm)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c
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δ (ppm)

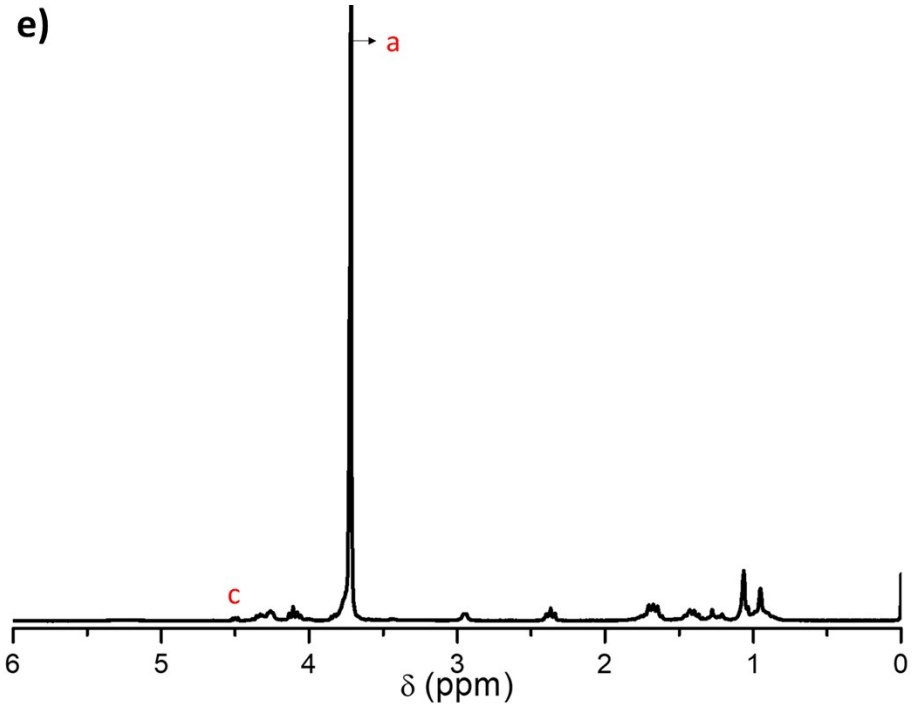
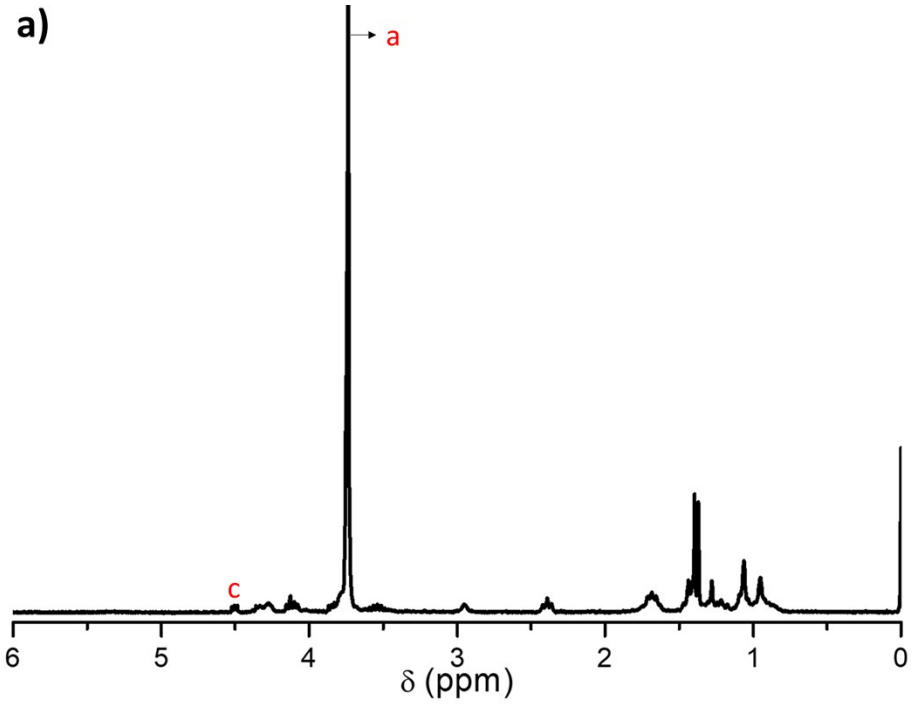


Figure S5. ^{1}H NMR spectra of HPU2_1 synthesized at 100°C under N_2 flow at a n_{DIPA}/n_{NCO} molar ratio of 1 and for a) 60 min, b) 120 min, c) 240 min, d) 480 min, and e) 960 min of reaction time and after the addition of trifluoracetic anhydride. “c” and “a” are the signals assigned to the PEG chain terminations and monomeric unit, respectively.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c
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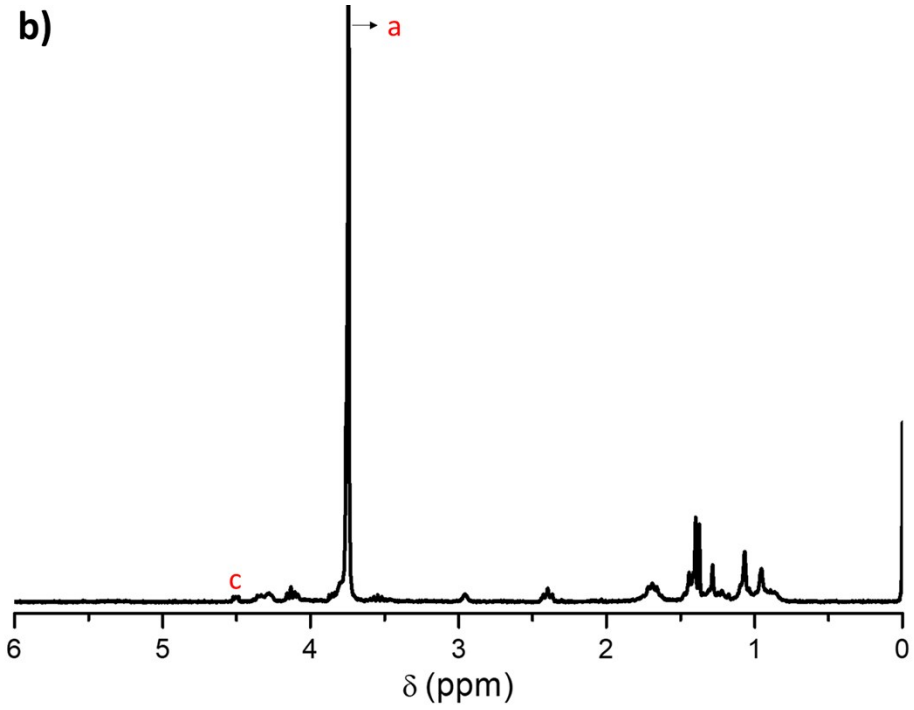
4
3
2
1
0
δ (ppm)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a
c
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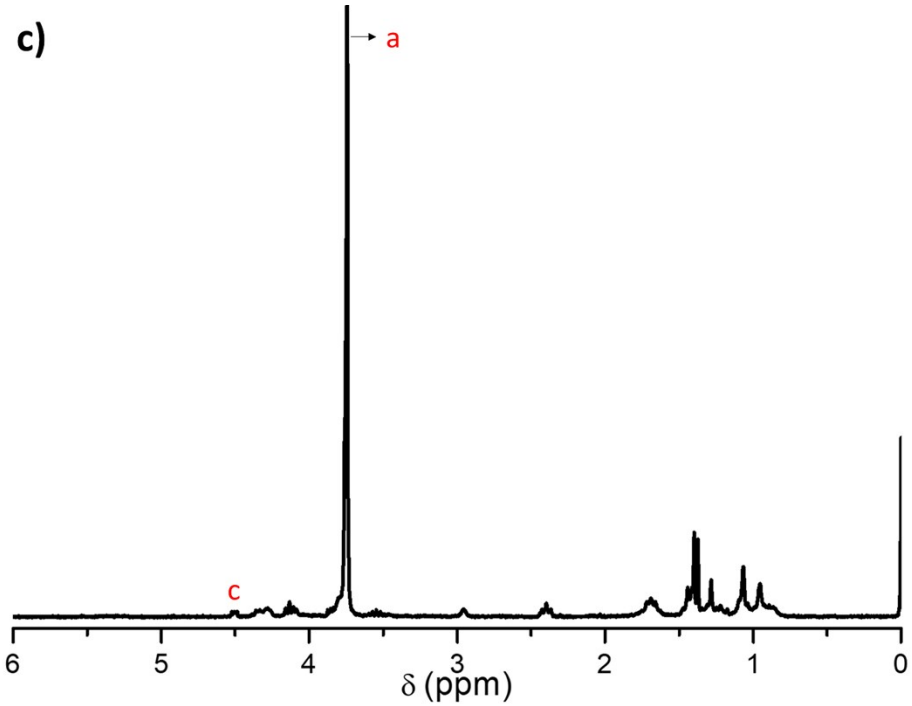
5
4
3
2
1
0
δ (ppm)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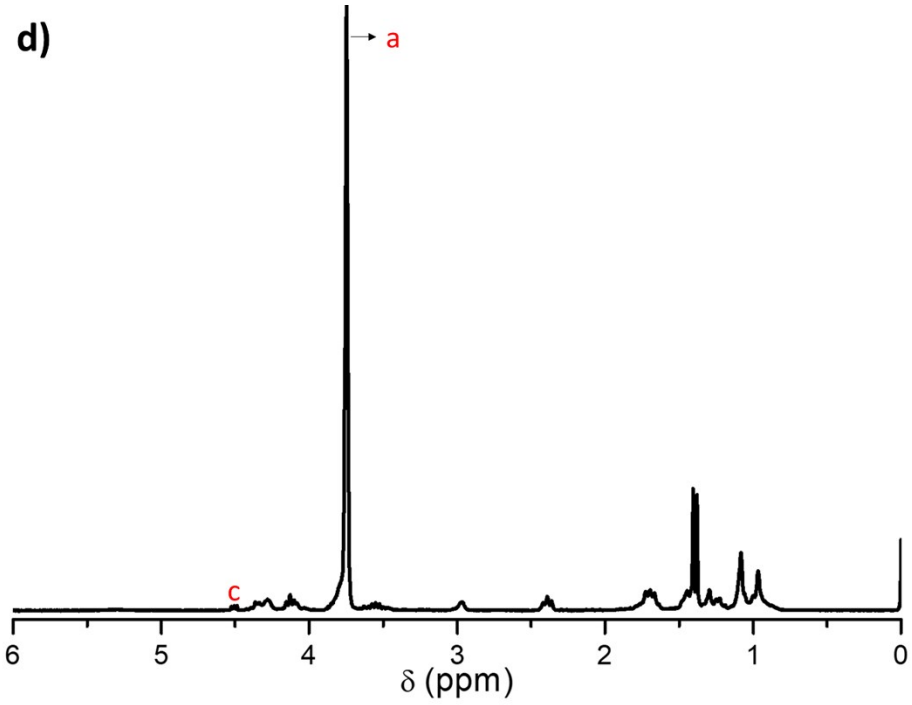
1
0
δ (ppm)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δ (ppm)

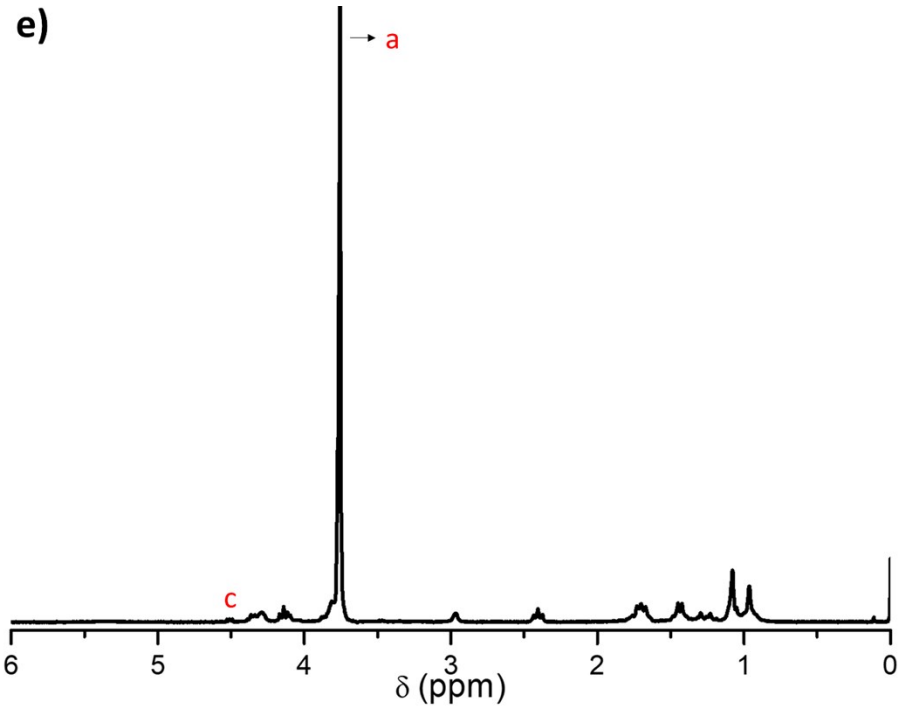
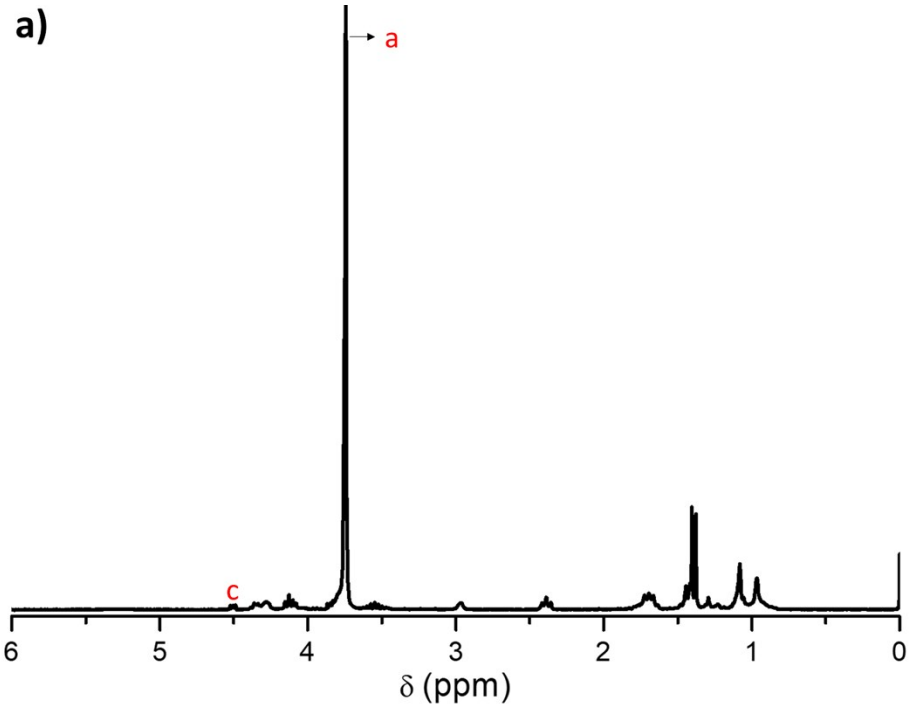


Figure S6. ^{1}H NMR spectra of HPU2_0.25 synthesized at 100°C under N_2 flow at a n_{DIPA}/n_{-NCO} molar ratio of 0.25 and for a) 30 min, b) 60 min, c) 120 min, d) 240 min, and e) 480 min of reaction time. “c” and “a” are the signals assigned to the PEG chain terminations and monomeric unit, respectively.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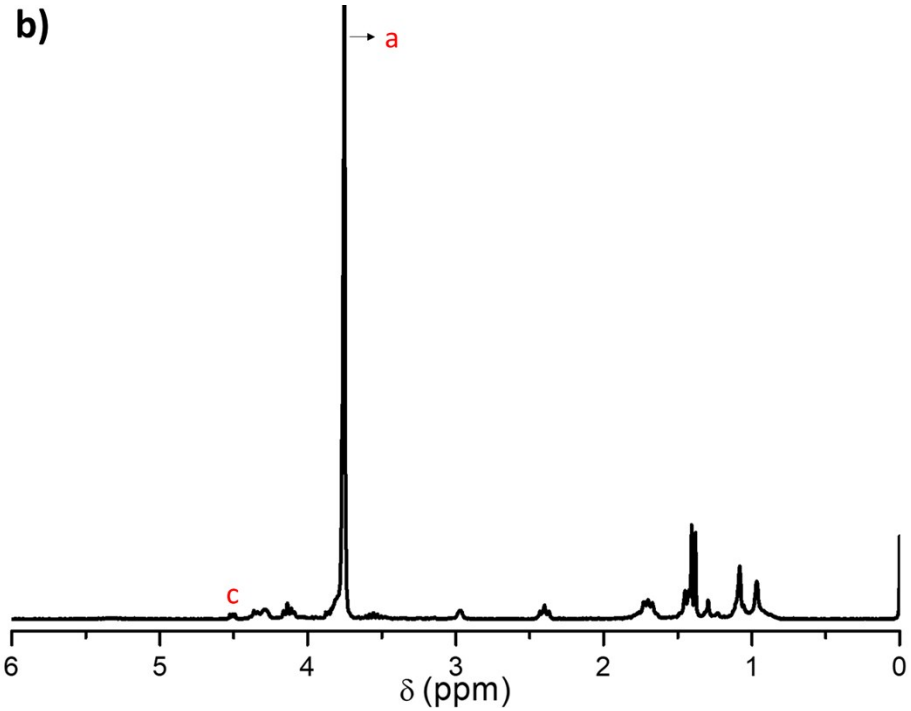
a
c
6
5
4
3
2
1
0
δ (ppm)


b)
a
c
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4
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2
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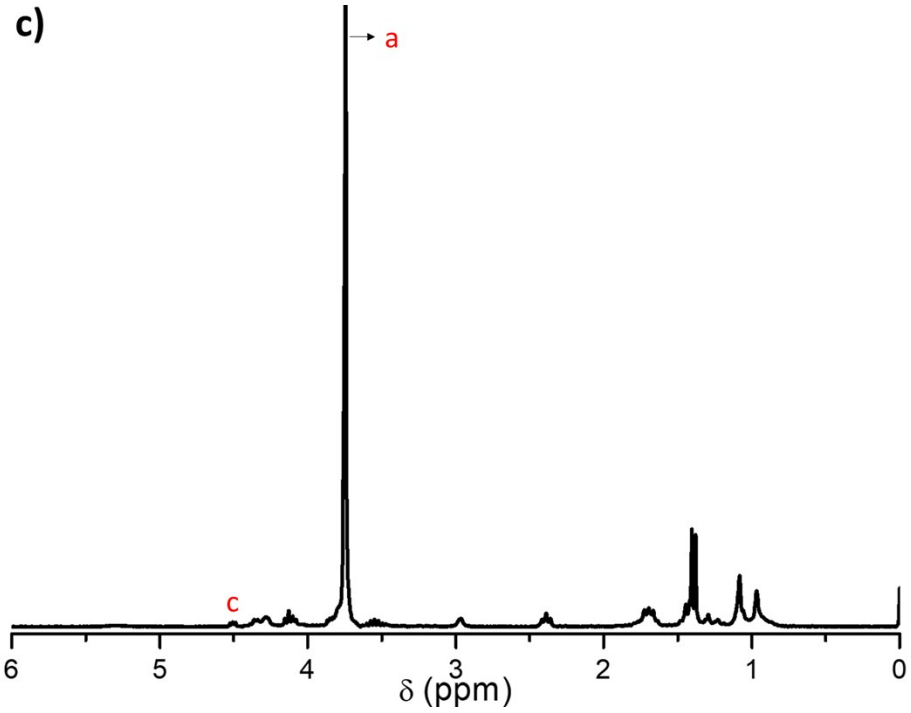
0
δ (ppm)


c)
a
c
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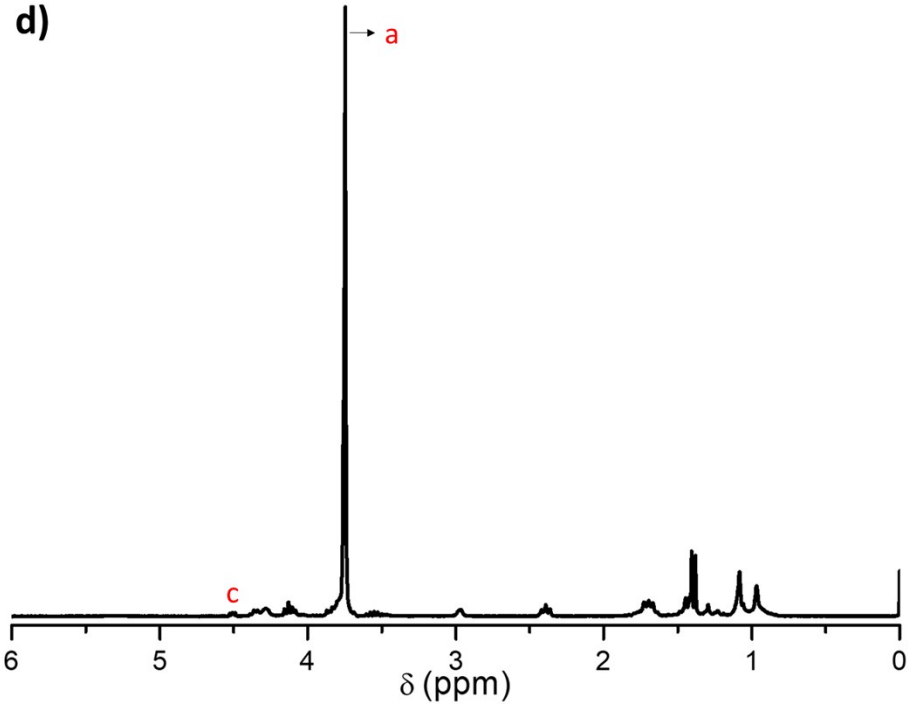
5
4
3
2
1
0
δ (ppm)


d)
a
c
6
5
4
3
2
1
0
δ (ppm)

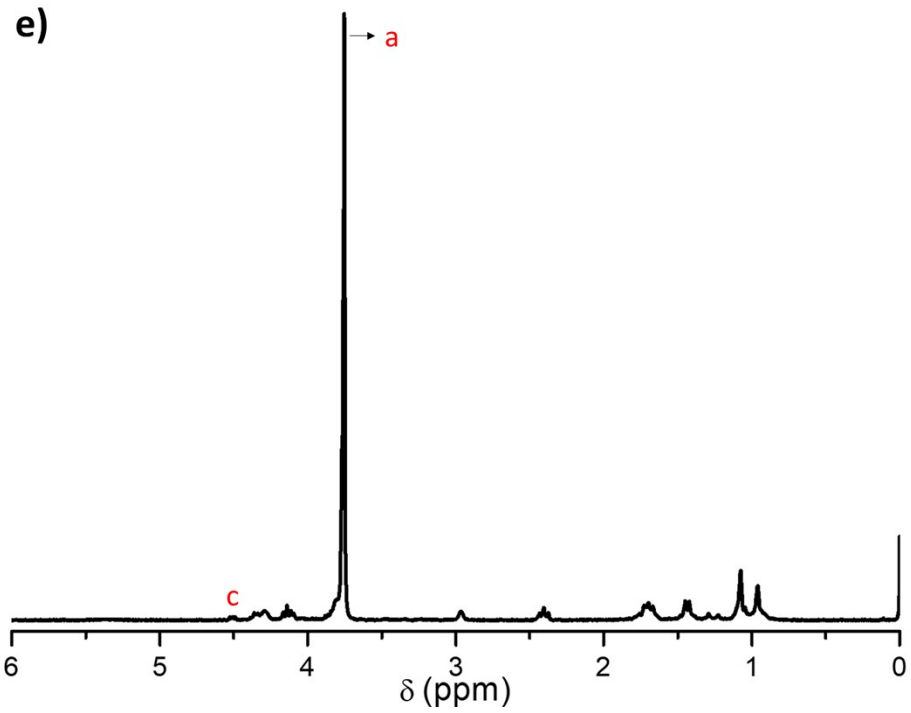


Figure S7. ^{1}H NMR spectra of HPU2_0.125 synthesized at 100°C under N_2 flow at a n_{DIPA}/n_{-NCO} molar ratio of 0.125 and for a) 20 min, b) 40 min, c) 60 min, d) 120 min, and e) 300 min of reaction time. “c” and “a” are the signals assigned to the PEG chain terminations and monomeric unit, respectively.

Section III: DSC data

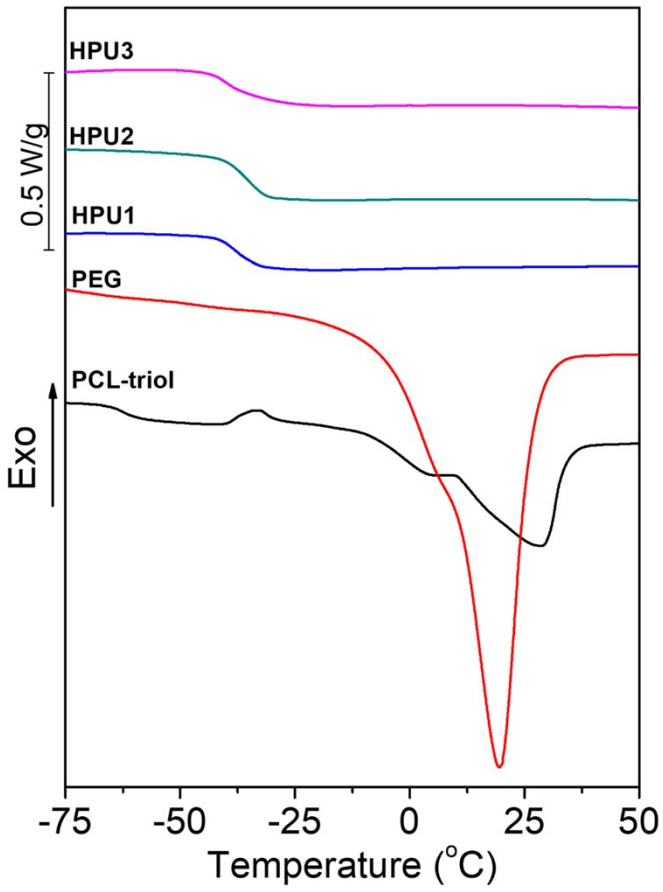


Figure S8. Second heating DSC curves of the HPUs and their precursors.

Section IV: SEC chromatograms

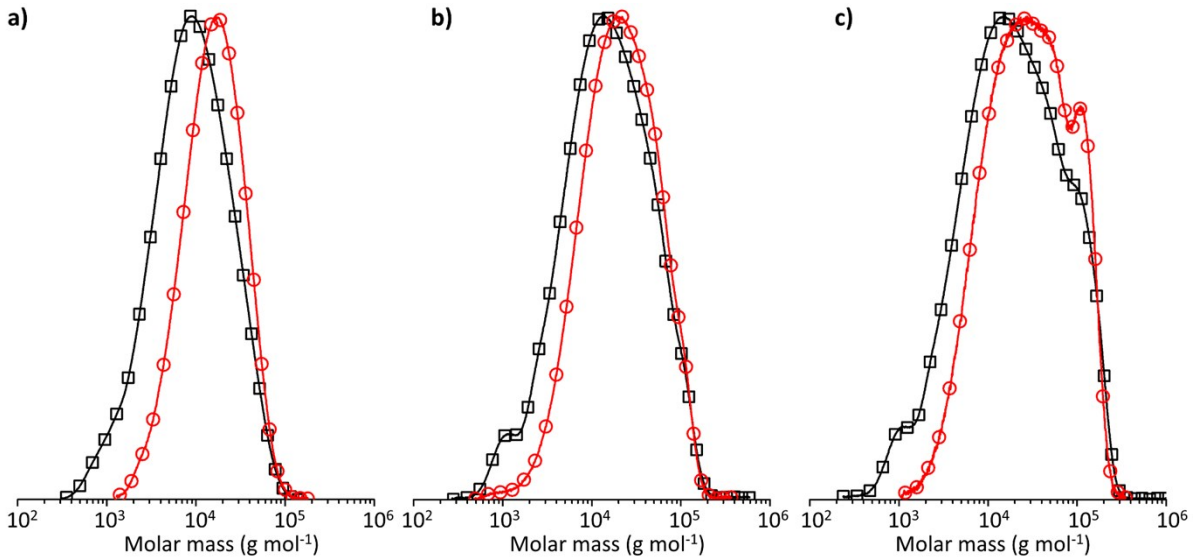


Figure S9. SEC chromatograms of a) HPU1, b) HPU2, and c) HPU3 before (□) and after (○) purification.

Section V: Evolution of the conversion and molar mass of HPU with reaction time

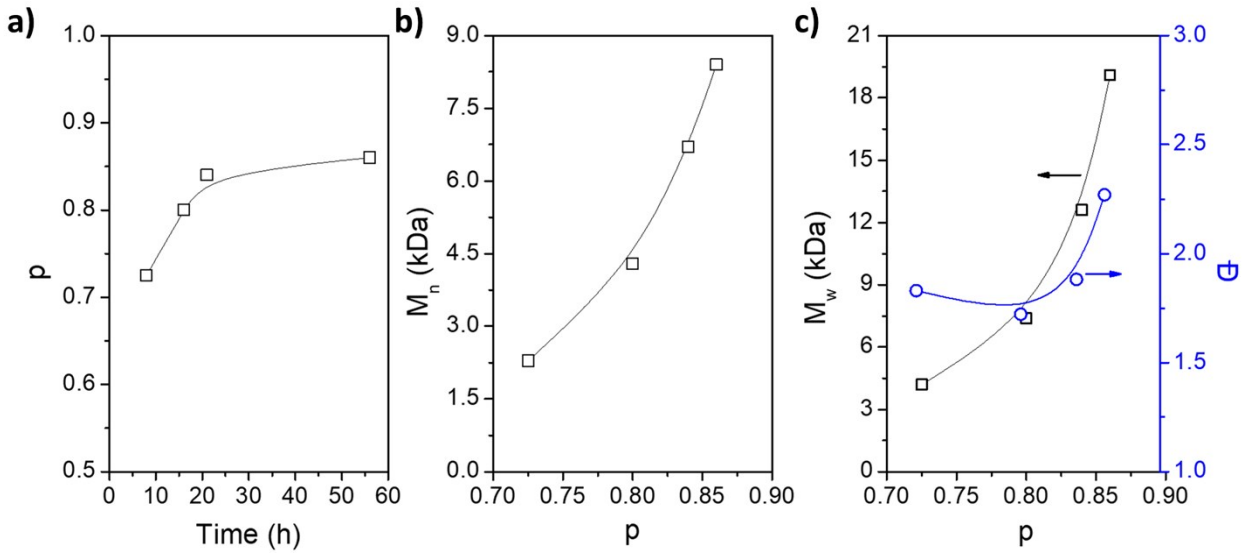


Figure S10. a) Conversion (p) versus time, b) M_n versus p, and c) M_w versus p for the HPU3_M_w series.

Section VI: Self-assembly of HPUs in aqueous media

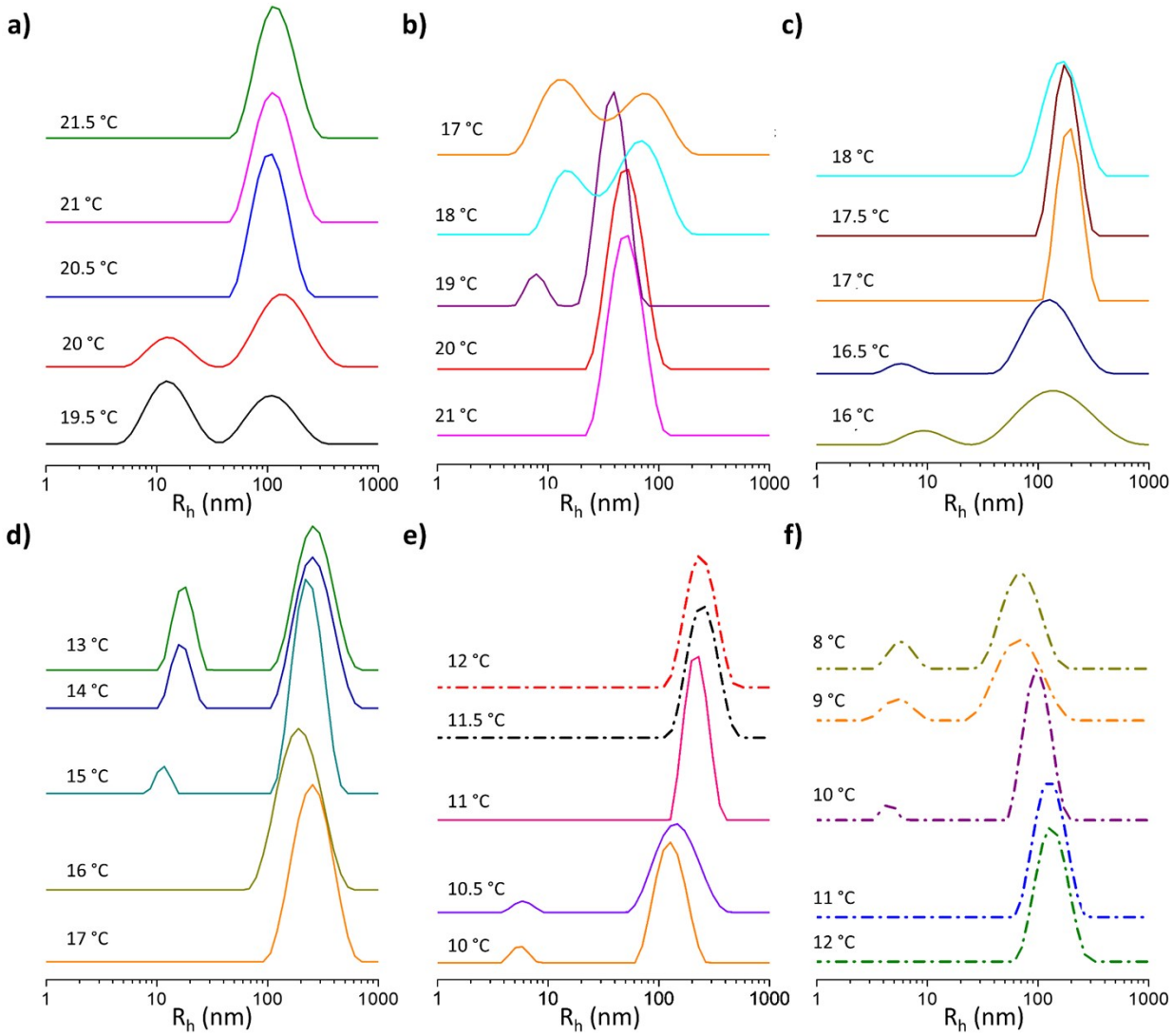


Figure S11. R_h distribution profile obtained by DLS for the HPU3_M_w series at 0.125 mg mL^{-1} in aqueous medium as a function of temperature for **a)** HPU3_4k - heating, **b)** HPU3_4k - cooling, **c)** HPU3_7k - heating, **d)** HPU3_7k - cooling, **e)** HPU3_13k - heating and **f)** HPU3_13k - cooling.