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Supplementary Information

for

Non-Isocyanate Poly(amide-hydroxyurethane)s from Sustainable Resources

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Synthesis of hydroxyurethane methylester. CC-ME (0.7 g, 3.0 mmol), DCM (10 mL), and 1-aminohexane (0.4 g, 4.0 mmol) were added into a 100 mL round-bottomed flask equipped with a magnetic stir bar. The reaction mixture was stirred at 40 °C for 3 h. After cooling back to room temperature, the reaction mixture was washed with 1 M HCl to remove excess amine. DCM was removed and product was washed with diethyl ether. Product was decanted off diethyl ether and dried in vacuo, yielding yellow viscous oil. HRMS (ES+): m/z calcd for $[M+H]^+$ 346.2588 g/mol; found 346.2602 g/mol.

Synthesis of bis(hydroxyurethane) dimethylester. CC-ME (3.0 g, 12.3 mmol) and 1,6-diaminohexane (0.7 g, 5.9 mmol) were added into a 100 mL round-bottomed flask equipped with a magnetic stir bar. The reaction mixture was stirred at 80 °C for 12 h, yielding viscous yellow oil. After cooling back to room temperature, 3 mL of DCM was added and stirred to dissolve the oil. The mixture was precipitated to a hexane-ether 2:6 mixture. The precipitant was dissolved in DCM and reprecipitated in hexane-ether 3:1 mixture. The precipitant was dried in vacuo, yielding a yellow wax-like solid-liquid mixture. Evaporation of half the decanted off solvent left white powder on the side of the beaker. The white powder was collected and dried in vacuo. The yellow wax contained both isomers; the white powder only contained the isomer with primary hydroxyl groups. Mass spectroscopy showed the same m/z for both products. HRMS (ES+): m/z calcd for $[M+H]^+$ 605.4013 g/mol; found 605.3989 g/mol.

Synthesis of hexanediamide diene or dodecanediamide diene. 9-DAME (25 g, 0.13 mol), 5 mol% $La(OTf)_3$ or TBD and 1,6-diaminohexane (6.3 g, 54 mmol) were added into a 250 mL round-bottomed flask equipped with a magnetic stir bar. The reaction mixture was melted at 80 °C and stirred for 5 h with slow nitrogen purge until the mixture solidified. The reaction was allowed to stir overnight. The resulted mixture was filtered and washed with MeOH. The solid was recrystallized from IPA and dried in vacuo, giving higher than 80% isolated yield. Dodecanediamide diene was synthesized using the same procedure with more than 80% isolated yield. Hexanediamide diene melting point was 128-130 °C. HRMS (ES+): m/z calcd for $[M+H]^+$ 421.3794 g/mol; found 421.3789 g/mol. Dodecanediamide diene melting point was 125-126 °C. HRMS (ES+): m/z calcd for $[M+H]^+$ 505.4733 g/mol; found 505.4719 g/mol.

Model compound reactions for hydroxylurethane formation and amidation. The well-known aminolysis of cylic carbonates was verified using CC-ME monomer and 1-aminohexane (Scheme S1).[1] The reaction finished in 3 h according to NMR spectroscopy. The purified product was an isomer mixture of hydroxyurethane methylester with 70% of secondary hydroxyls and 30% of primary hydroxyls, determined through ^1H NMR spectroscopy (Figure S3). Secondary hydroxyls dominated due to the O=C-O single bond length difference on the cyclic carbonate.[1] The ratios reported in literature varied from 85/15 to 56/44, depending on solvents, catalysts, and amines.[1-3] FTIR also revealed the wavenumber shift of the signature absorption peak of carbonyls when cyclic carbonates converted to urethanes (Figure S5). CC-ME was also reacted with 1,6-

diaminohexane to obtain bis(hydroxyurethane) dimethylester, yielding three isomers (Scheme S2). The isomer with only primary hydroxyls was isolated and used as reference to correctly assign proton and carbon peaks in NMR spectroscopy (Figure S3,4,6,7). Secondly, amidation of ester is generally problematic due to low reactivity of the esters.[4] Lanthanum triflate and TBD were proved to be effective catalyst for quantitative amidation of methyl ester with efficient byproduct removal using constant nitrogen purge (Scheme S3).[5,6] Both 1,6-diaminohexane and 1,12-diaminododecane reacted with 9-DAME quantitatively at 80 °C in bulk. Mass spectroscopy and NMR spectroscopy confirmed the structure and purity of the produced diamide diene (Figure S8).

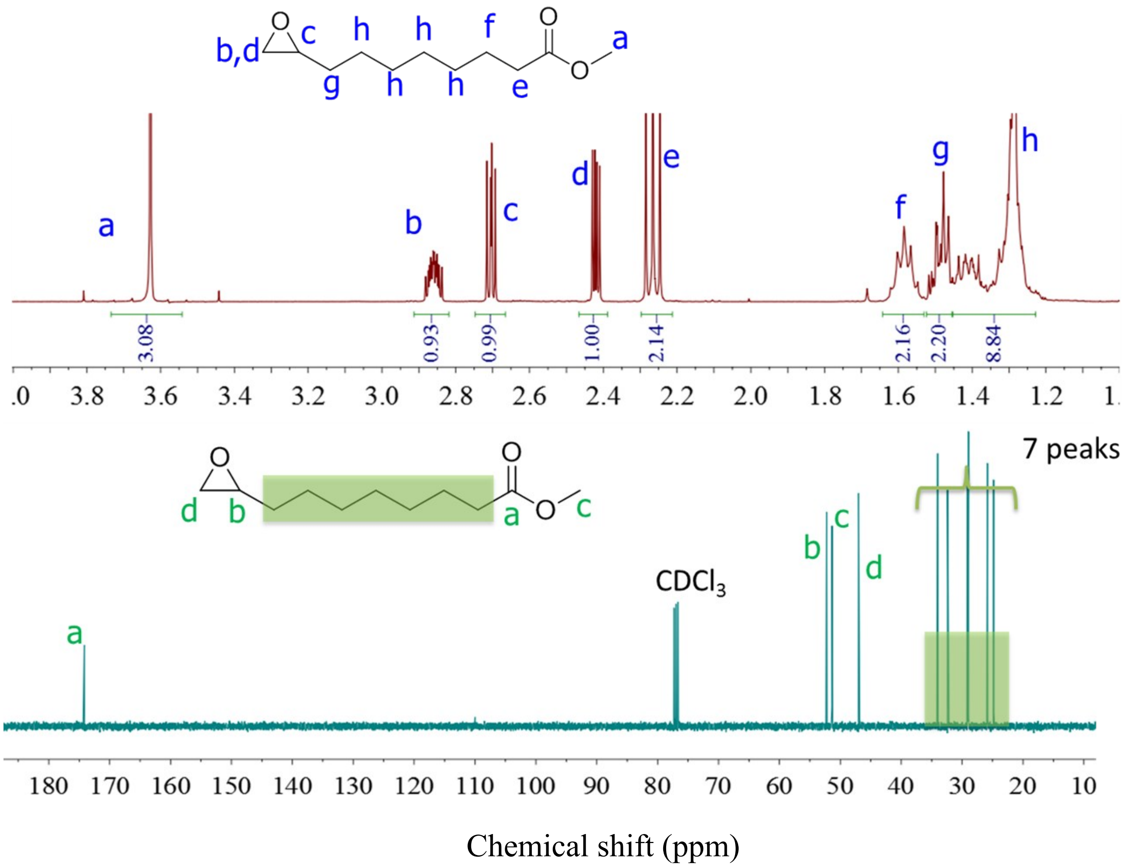


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of methyl 9,10-epoxydecanoate.

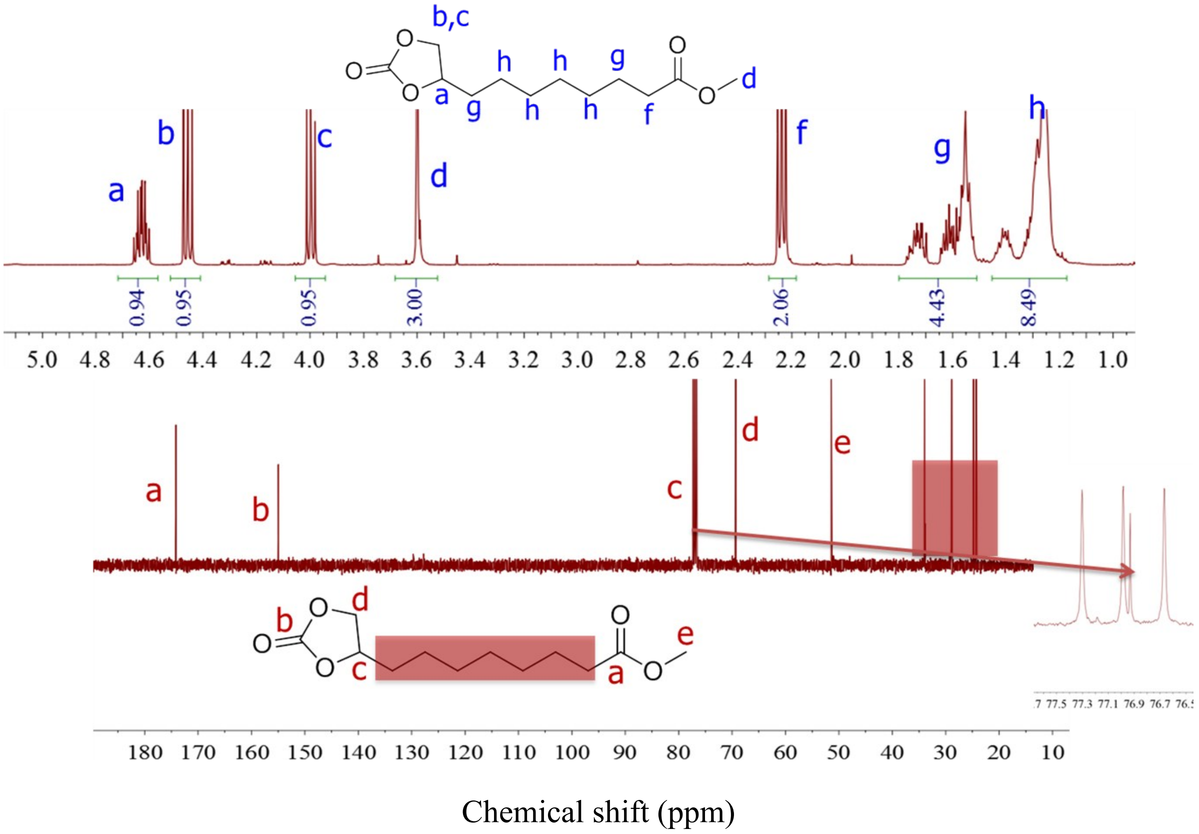
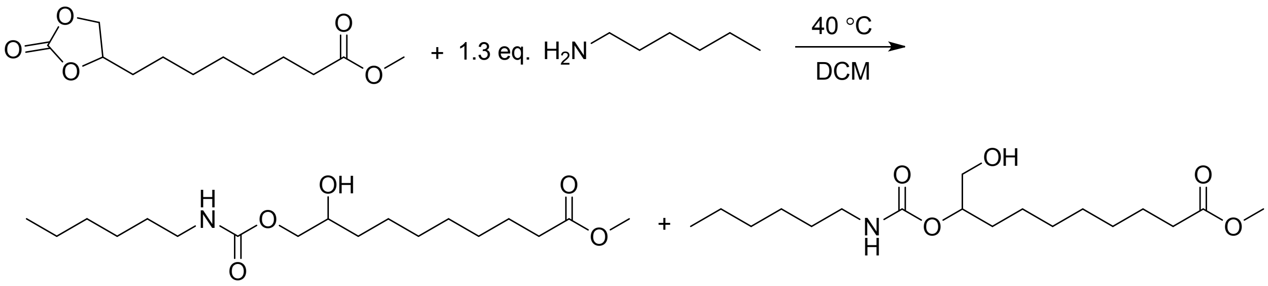


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of CC-ME monomer.



Scheme S1. Model compound reaction between CC-ME with 1-aminohexane, generating isomer mixture of hydroxyurethane methylester with primary and secondary hydroxyl groups.

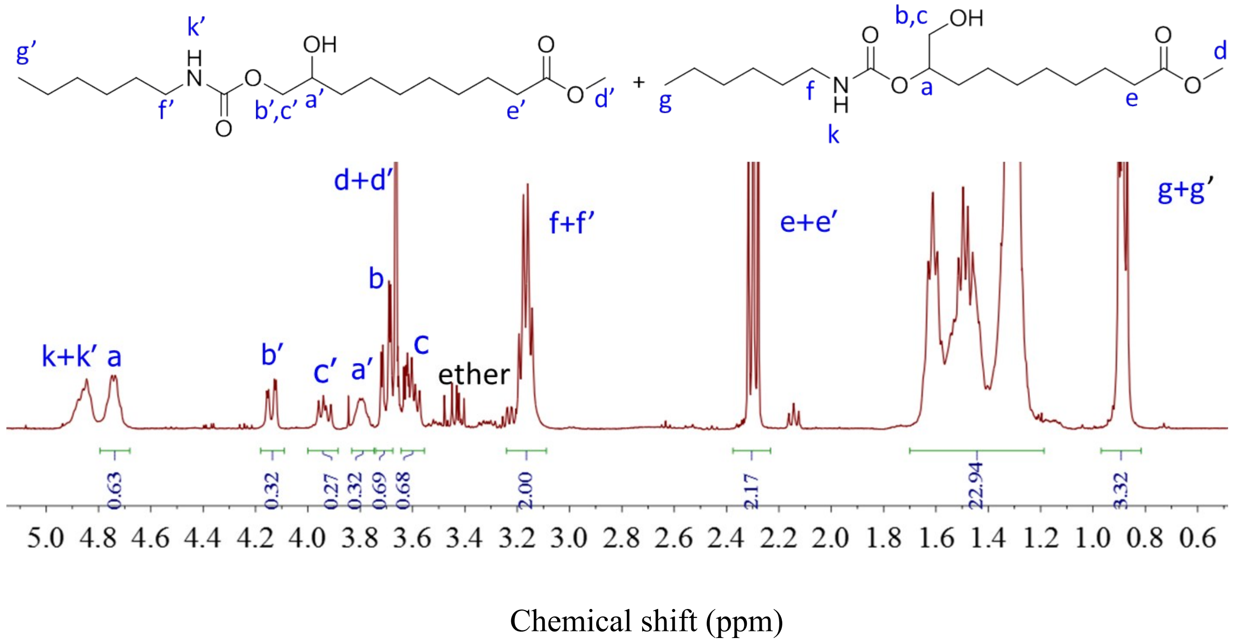


Figure S3. ^{1}H NMR spectrum of hydroxyurethane methylester isomer mixture.

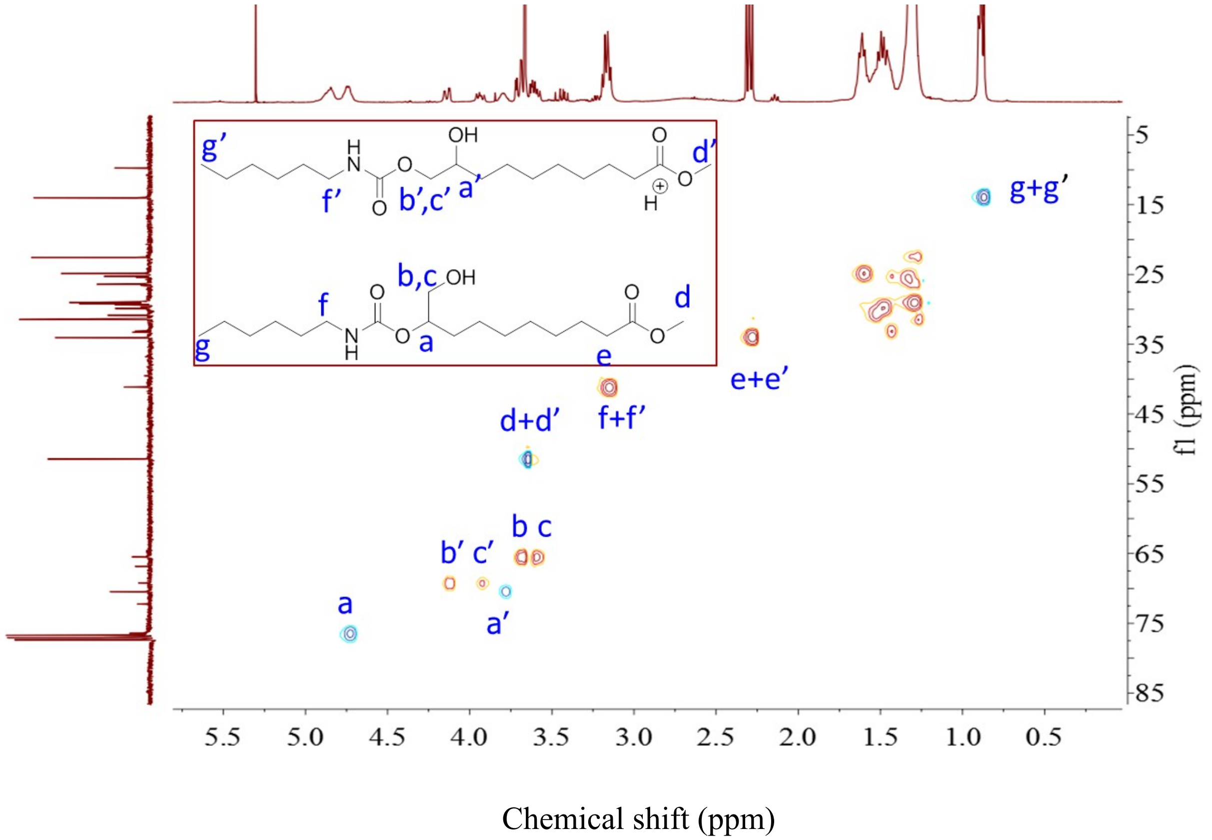


Figure S4. HSQC 2D NMR spectrum of the mixture of hydroxyurethane methylester isomers with primary and secondary hydroxyl groups.

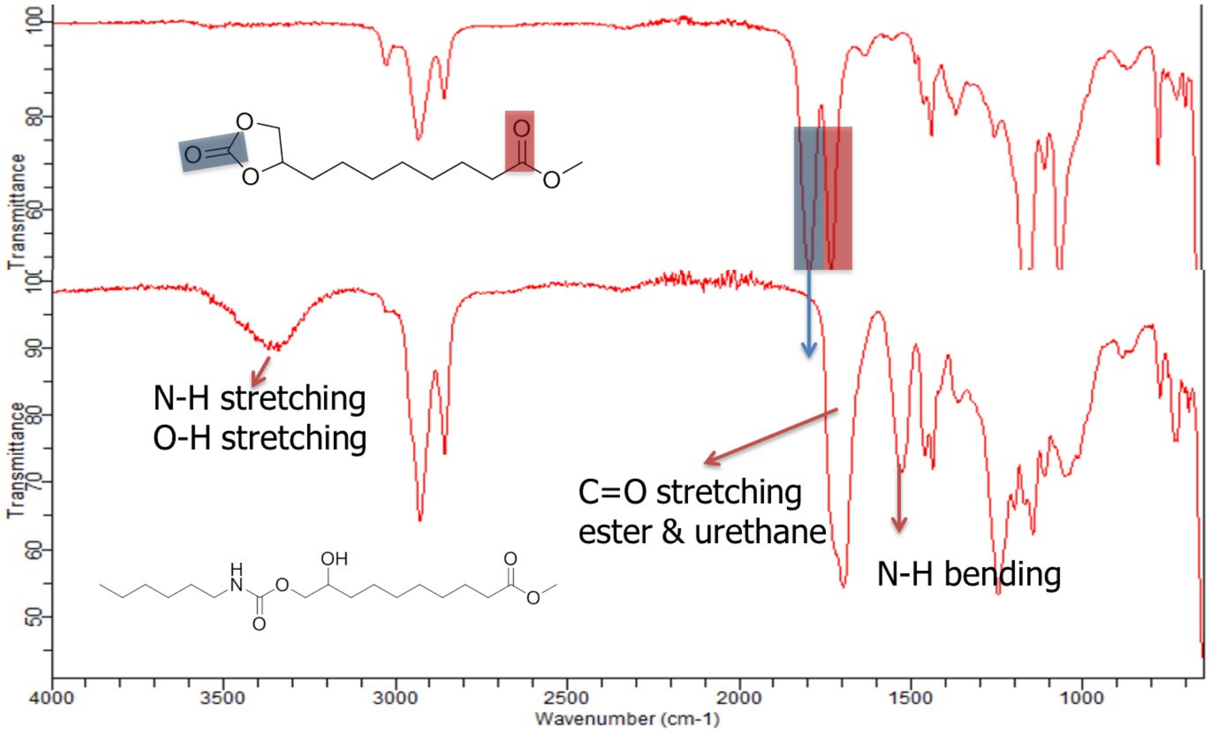
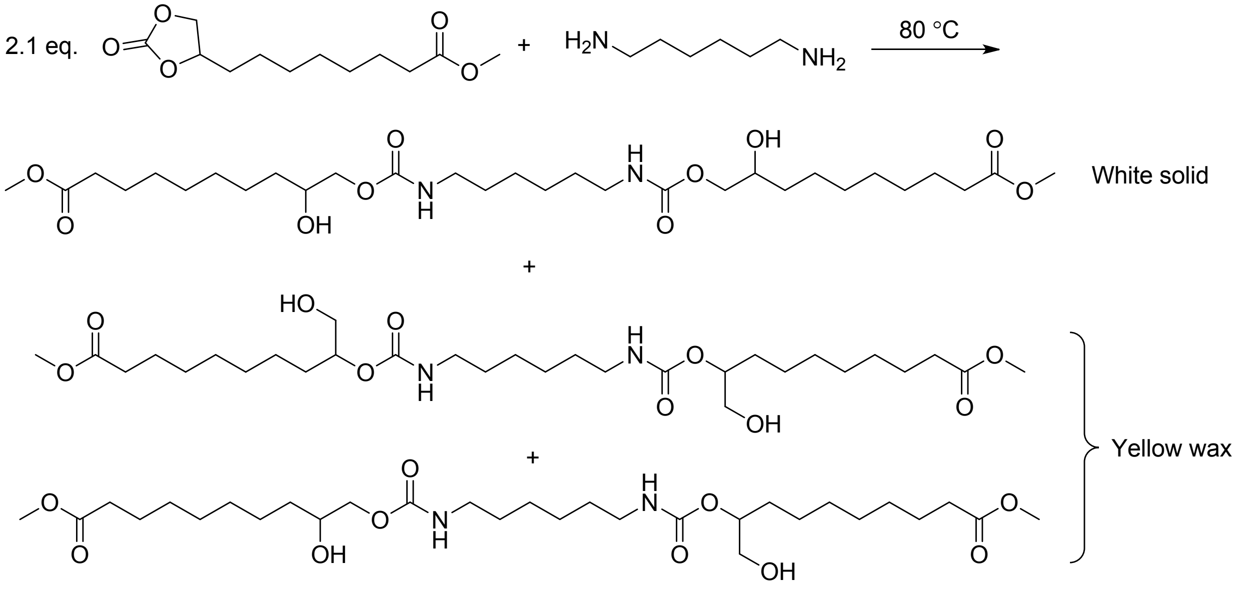


Figure S5. FTIR spectra of CC-ME and bis(hydroxyurethane) dimethylester.



Scheme S2. Model compound reaction between CC-ME with 1,6-diaminohexane, generating isomer mixture of bis(hydroxyurethane) dimethylester with primary and secondary hydroxyl groups, fractionated using percipitation.

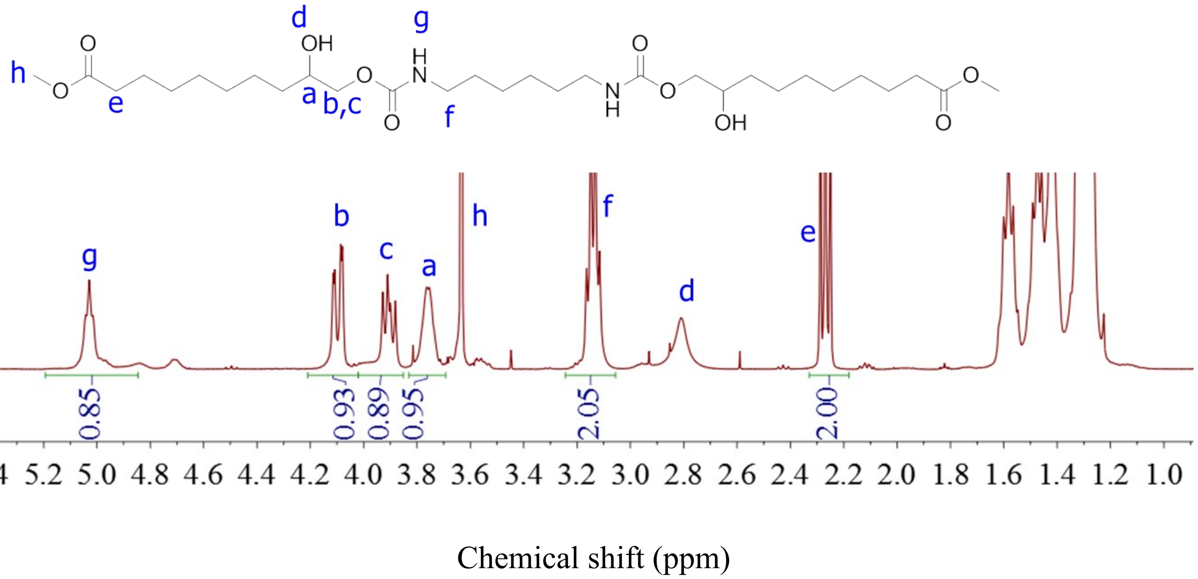


Figure S6. ^{1}H NMR spectrum of isolated bis(hydroxyurethane) dimethylester isomer with secondary hydroxyl groups.

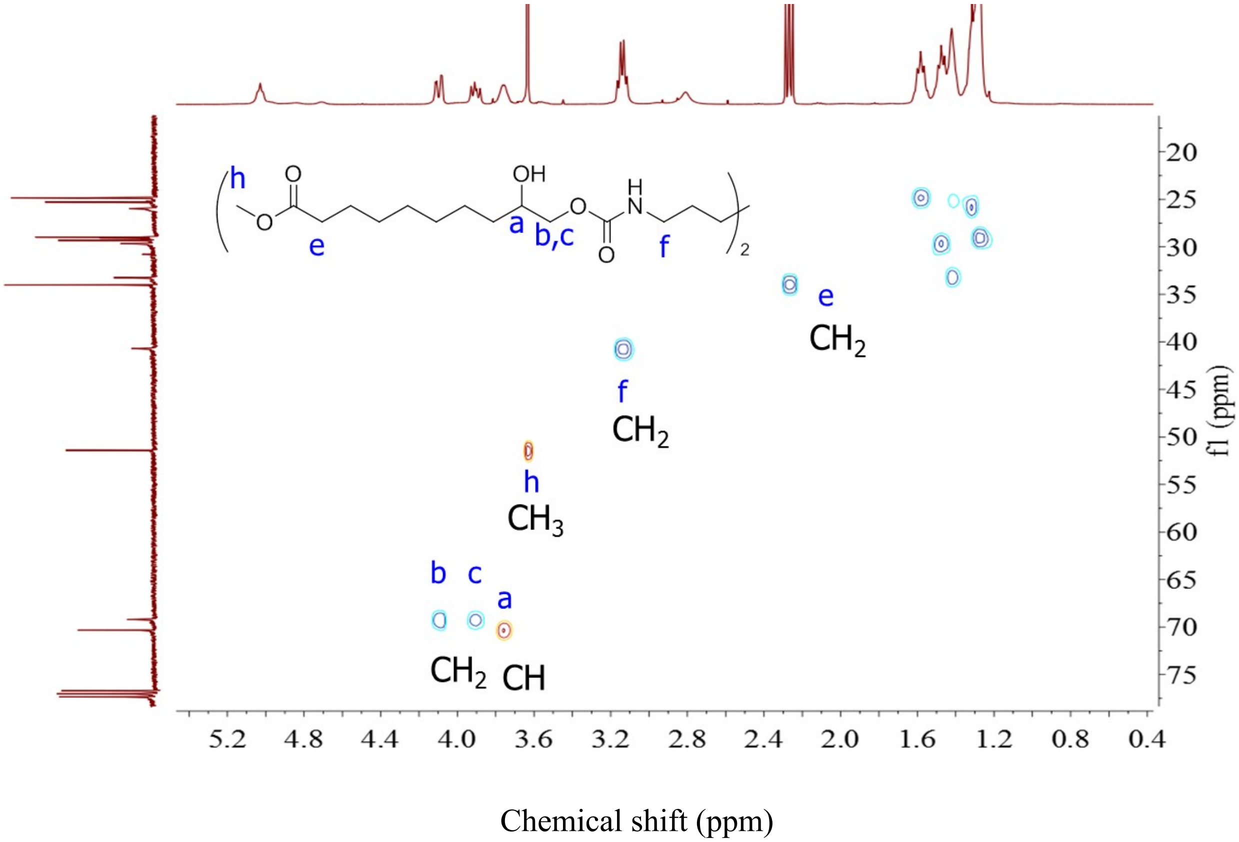
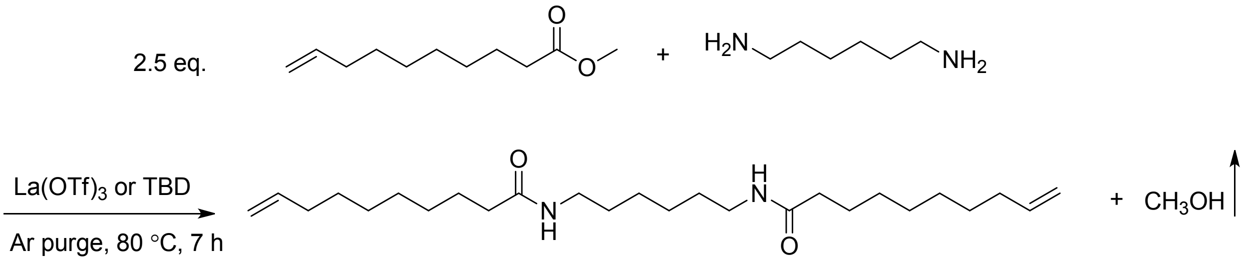


Figure S7. HSQC 2D NMR spectrum of isolated bis(hydroxyurethane) dimethylester with secondary hydroxyl groups.



Scheme S3. Model amidation reaction between 2 equivalent of 9-DAME with 1 equivalent of 1,6-diaminohexane, generating a hexanediamide diene.

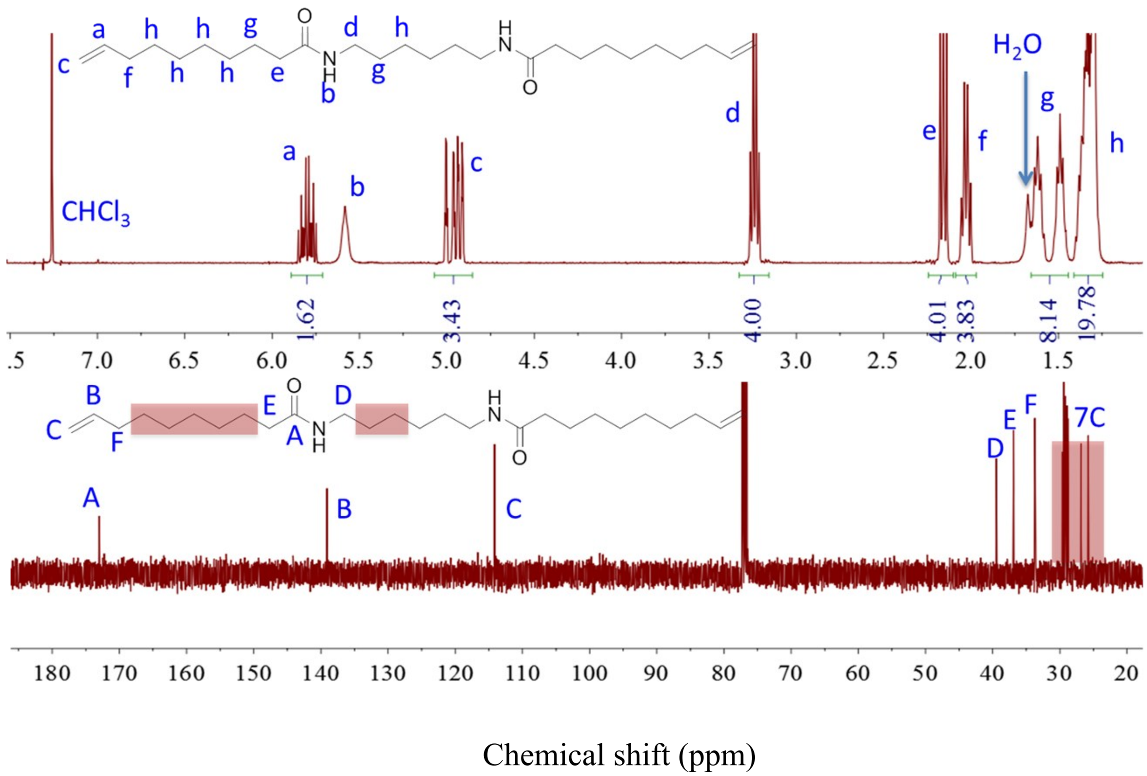


Figure S8. ^{1}H and ^{13}C NMR spectrum of hexanediamide diene.

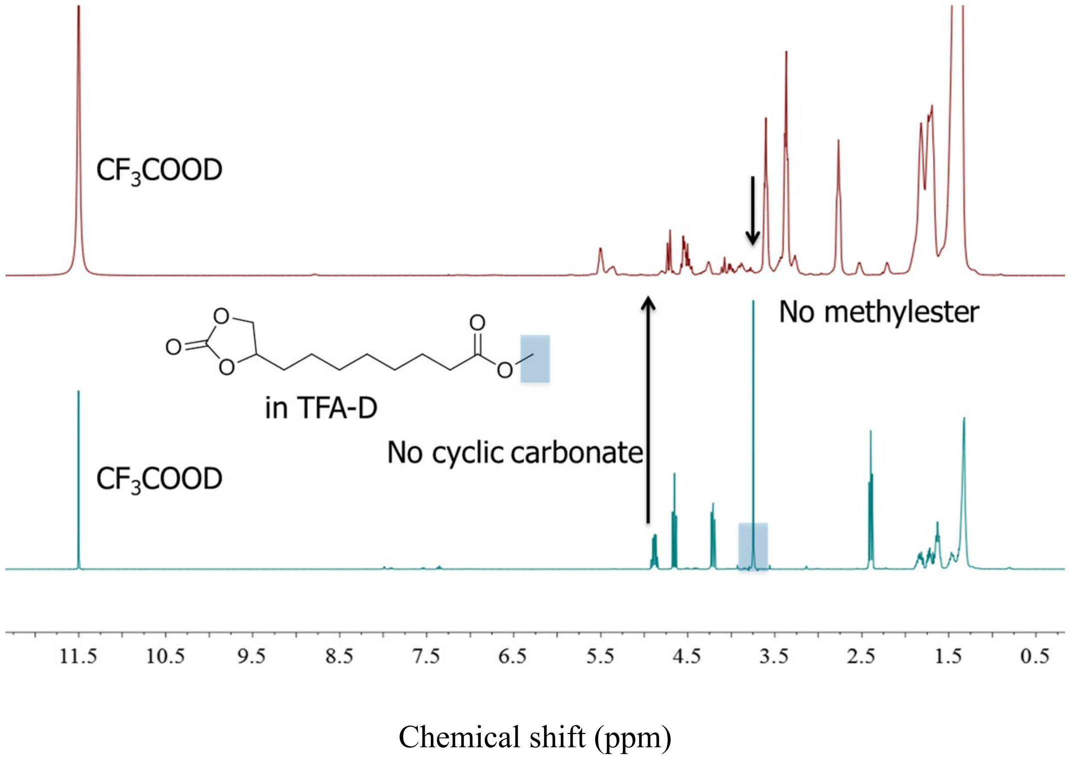


Figure S9. ^{1}H NMR spectra overlay of PA$_{12}$HU and CC-ME monomer in deuterated TFA, demonstrating full conversion of cyclic carbonate and methylester groups.

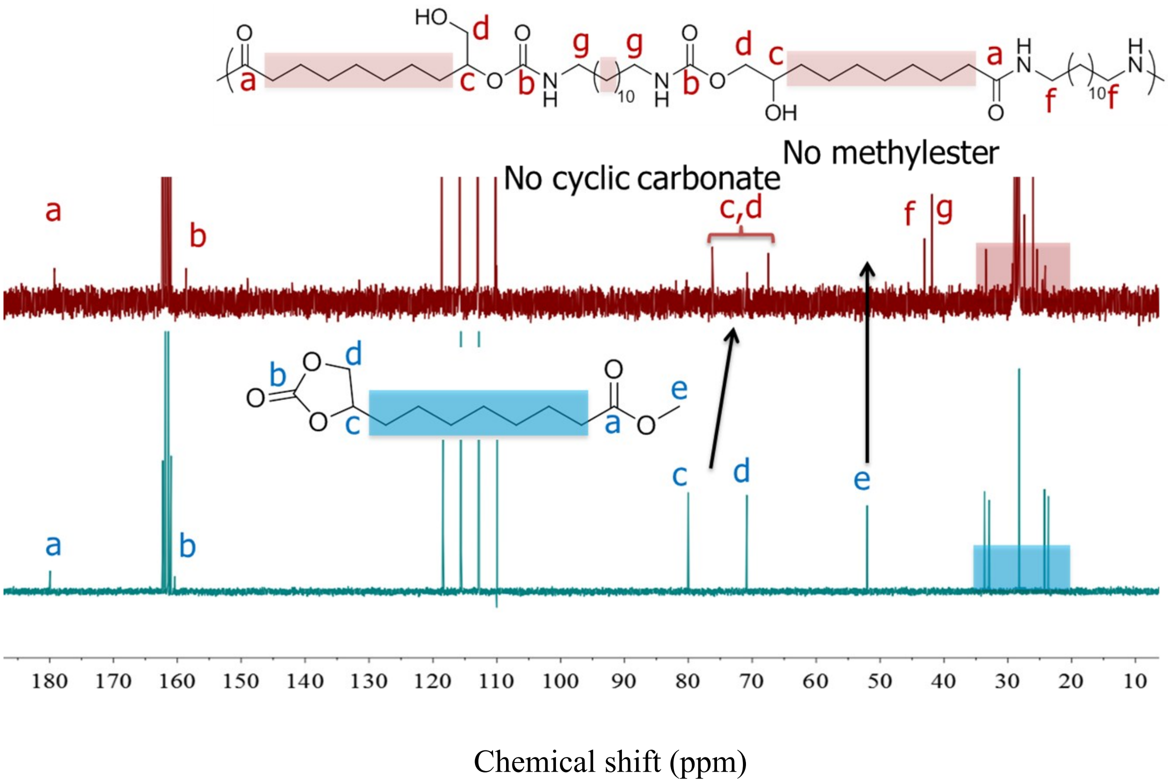


Figure S10. ^{13}C NMR spectra overlay of PA$_{12}$HU and CC-ME monomer in deuterated TFA, demonstrating full conversion of cyclic carbonate and methylester groups.

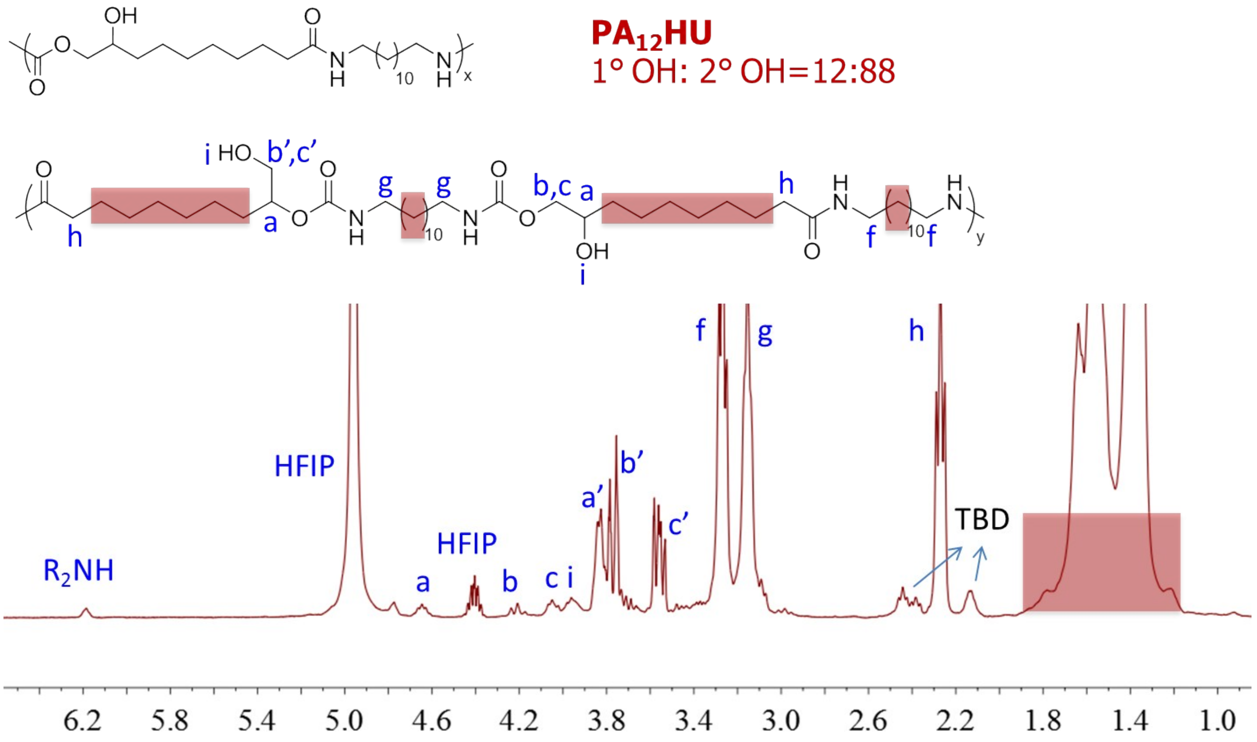


Figure S11. ^{1}H NMR spectrum of PA$_{12}$HU.

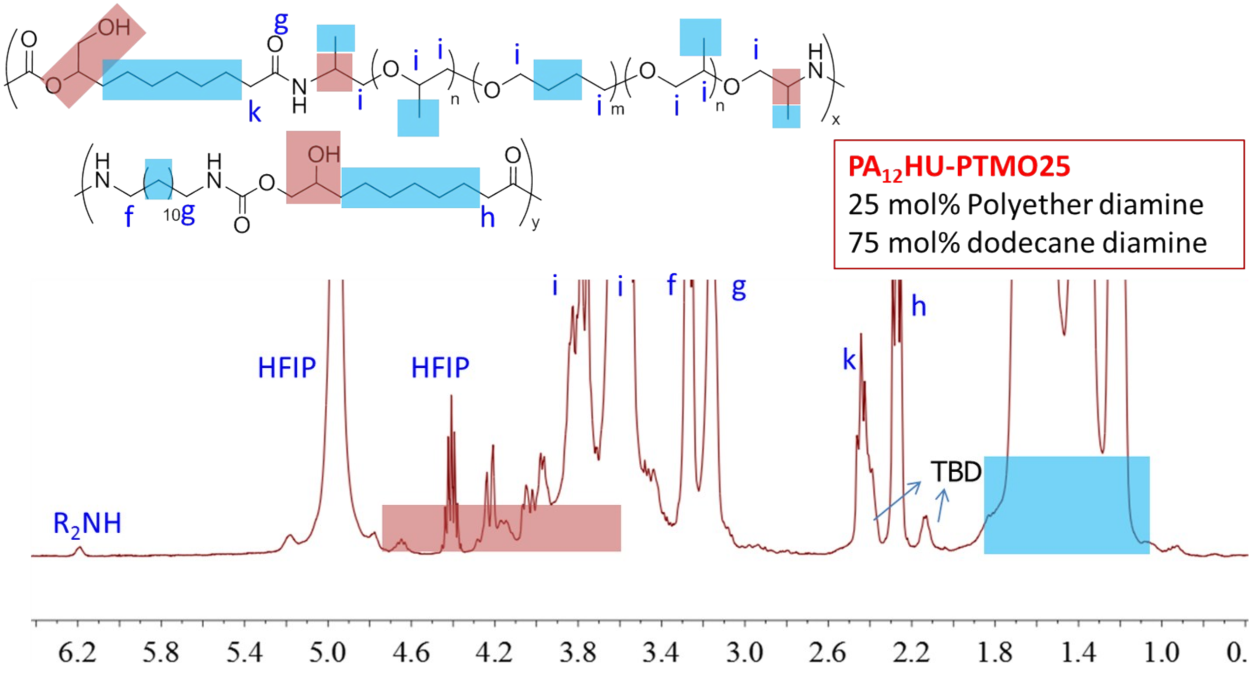
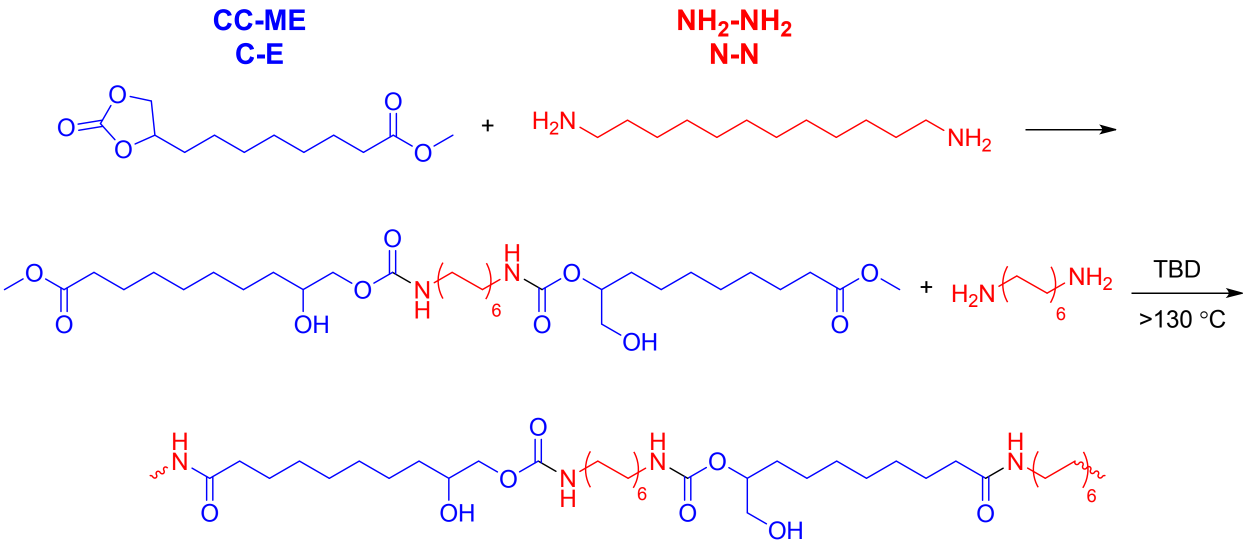


Figure S12. ^{1}H NMR spectrum of PA$_{12}$HU-PTMO25.



-NE-CN-NC-EN-

Scheme S4. Formation of the E-CN-NC-EN-N repeating unit in the structure of $PA_{12}HU$ -(C-EN-N)- and -(E-CN-NC-EN-N)-. The x/y ratio of the two isomers in Scheme 2 could not be determined using ^{1}H NMR spectroscopy or other available techniques, as the resonance peaks of the protons on both repeating units were overlapping. The longer repeating unit of E-CN-NC-EN-N formed due to different reaction kinetics of the amidation reaction and the ring-opening reaction of cyclic carbonate, shown in Scheme S4. The hydroxyurethane units started to form below 130° C, while the amidation reaction primarily occurred above 130° C, the melting temperature of the catalyst TBD in a melt polymerization. However, the actual conversions of the amidation and hydroxyurethane formation were challenging to monitor using *in-situ* spectroscopic methods as the polymerization was carried out in the melt. The ratio of two repeating units should not significantly affect the physical properties of resulting PAHU polymers.

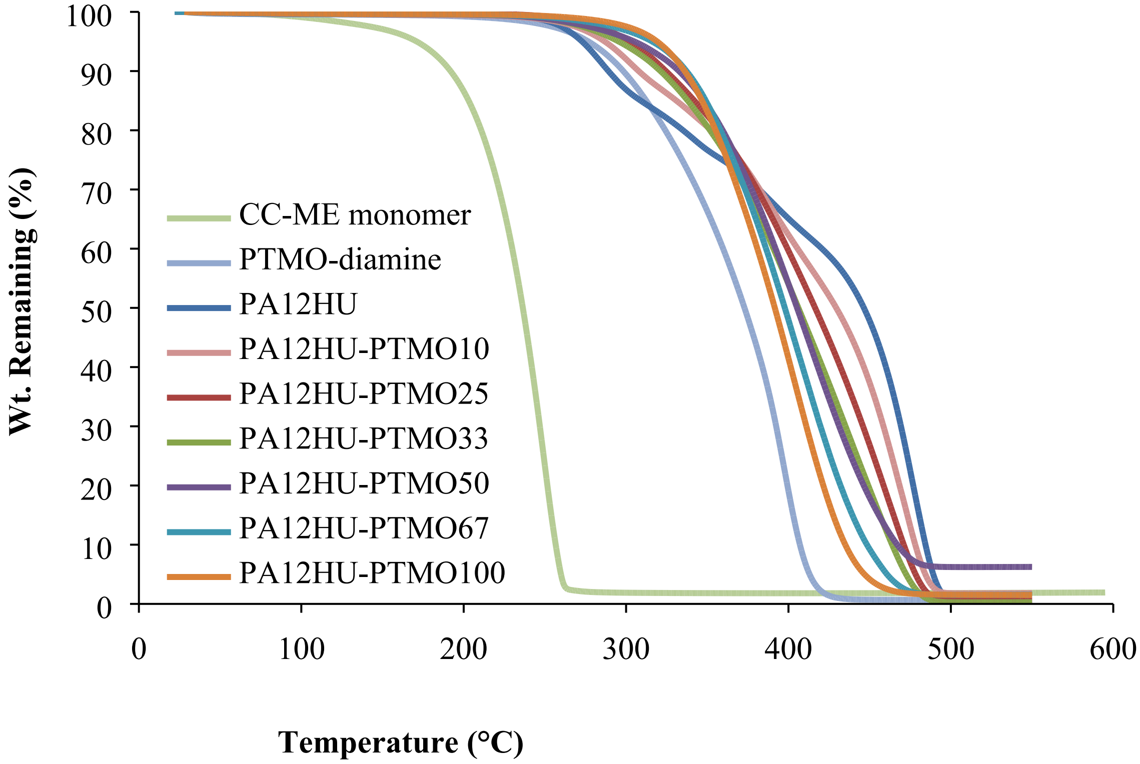


Figure S13. TGA thermograms of nonsegmented $PA_{12}HU$ and segmented $PA_{12}HU$-PTMOs, compared with PTMO-diamine precursor and CC-ME monomer under nitrogen purge.

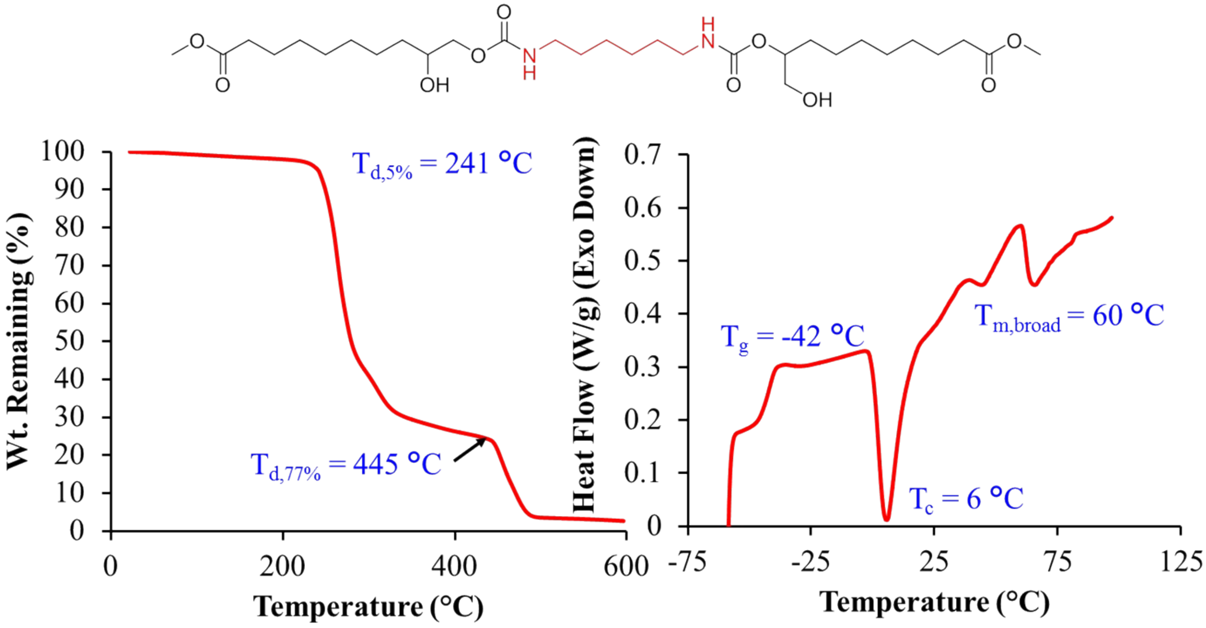


Figure S14. Thermal properties of the model compound bis(hydroxyurethane) dimethylester.

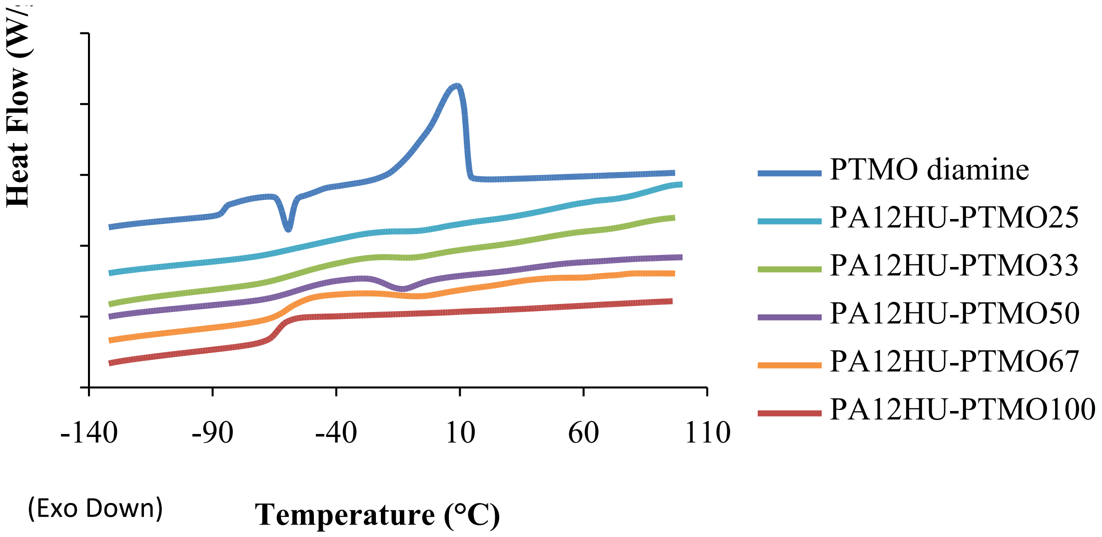


Figure S15. Cryo DSC traces of segmented $PA_{12}HU$-PTMOs, compared with PTMO-diamine 1 kDa. Second heat reported with 10 °C/min heating rate after quench cooling from 100 °C.

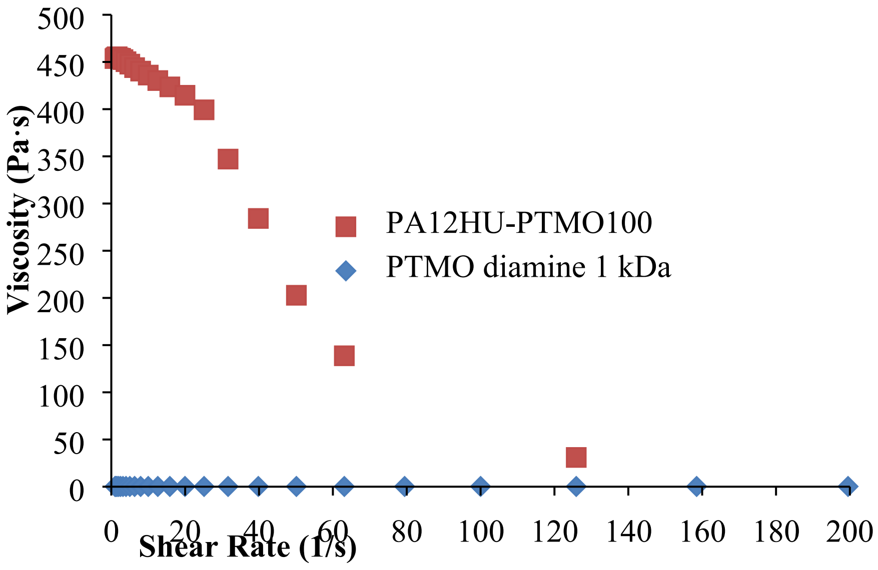


Figure S16. Shear rate sweep of $PA_{12}HU$-PTMO100 and 1 kDa PTMO diamine.

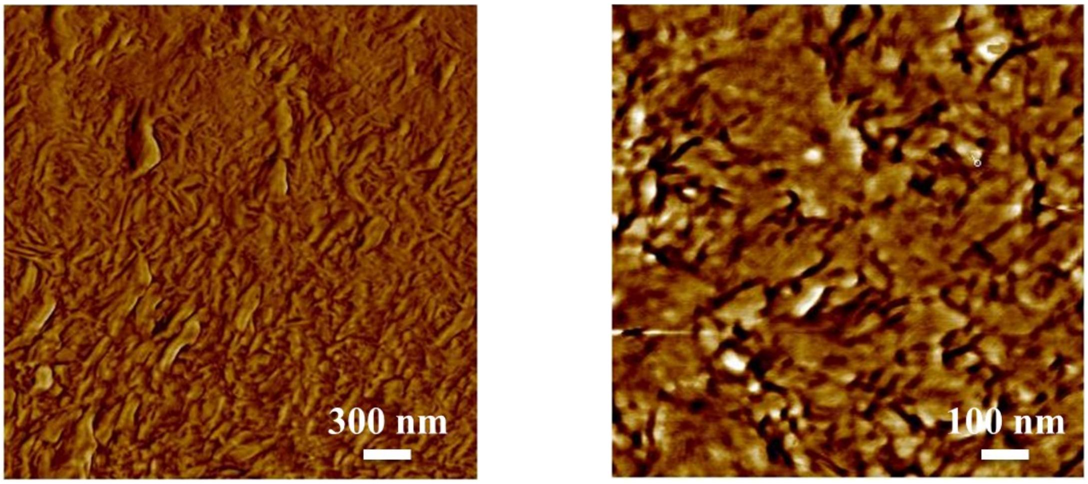


Figure S17. AFM tapping mode phase image of non-segmented $PA_{12}HU$.

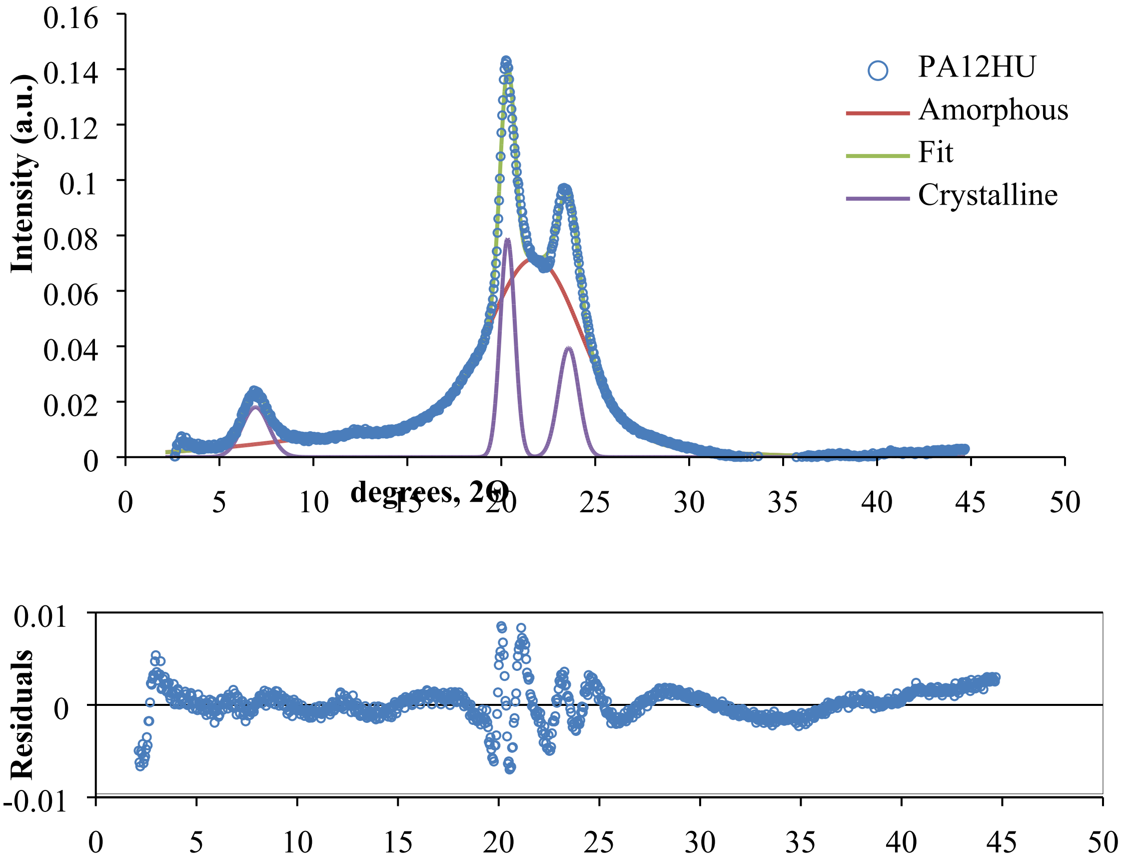


Figure S18. Peak deconvolution and residuals of the WAXD profile of non-segmented $PA_{12}HU$ using Guassian and Lorentzian functions.

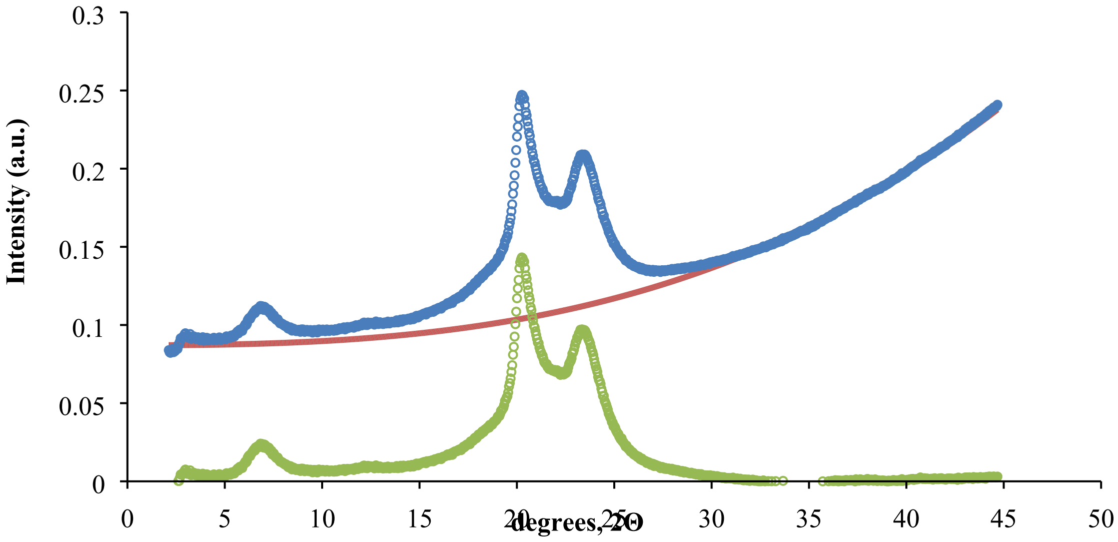


Figure S19. Baseline correction of the WAXD profile of non-segmented $PA_{12}HU$.

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