

Electronic Supplementary Information for

**Synthesis of Self-Healable Waterborne Isocyanate-Free
Poly(hydroxyurethane)-Based Supramolecular Networks by
Ionic Interactions**

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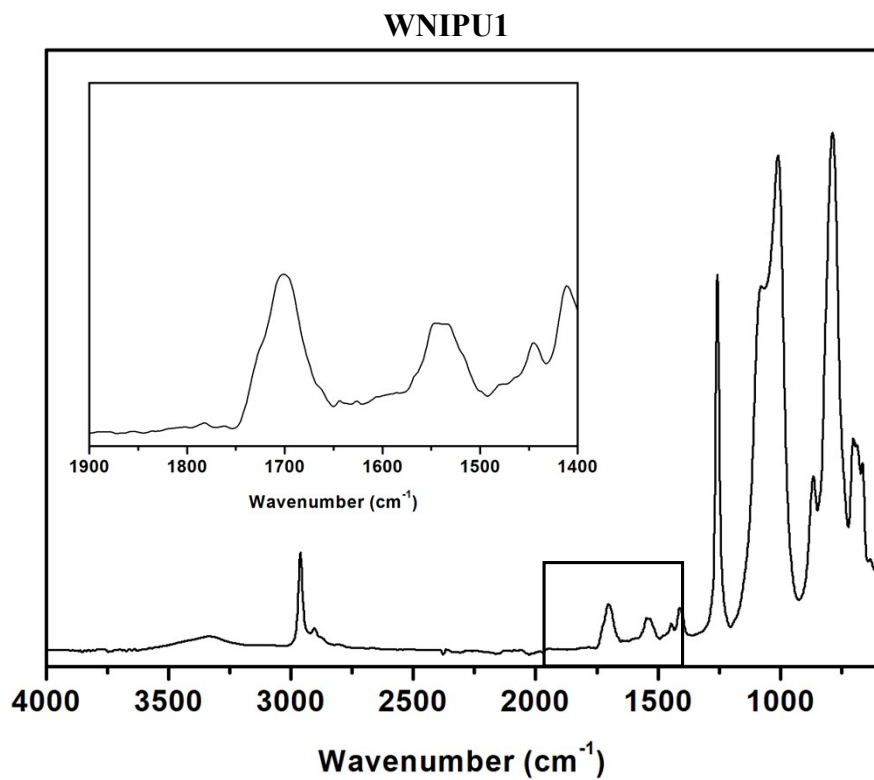


Figure S1. FTIR spectrum of WNIPU1.

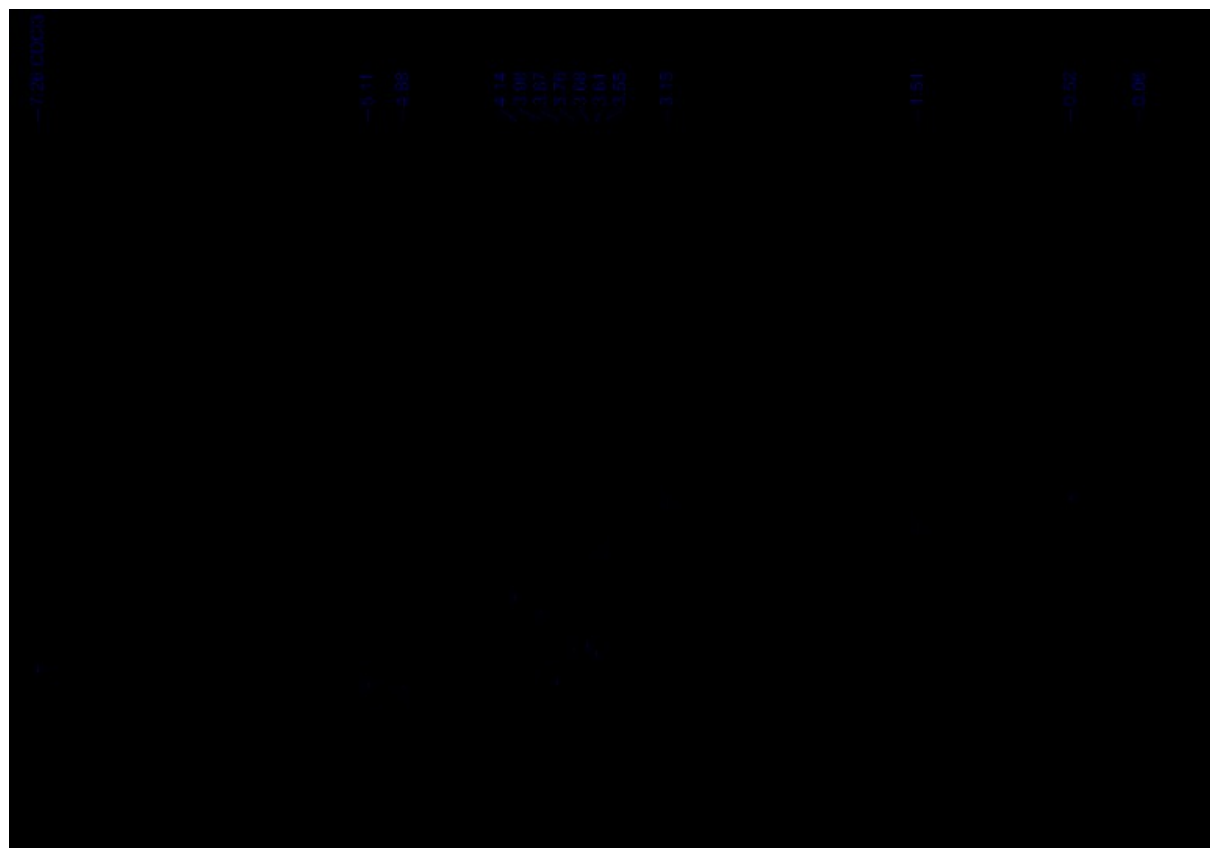


Figure S2. ^1H NMR of WNIPU1 (100-0 ratio), (300 MHz, CDCl_3) δ (ppm) = 5.11 (bs, CHOH), 4.88 (bs, $\text{CHO}(\text{CO})\text{N}$), 4.14 (m, $\text{CH}_2\text{O}(\text{CO})\text{N}$), 3.98 (m, CHCH_2O), 3.87 (m,

CHOH), 3.76 (m, CH₂CHCH₂O), 3.68-3.55 (m, CH₂OH), 3.15 (q, CH₂NH), 1.51 (quintuplet, SiCH₂CH₂CH₂NH), 0.52 (t, SiCH₂), 0.06 (s, SiCH₃).

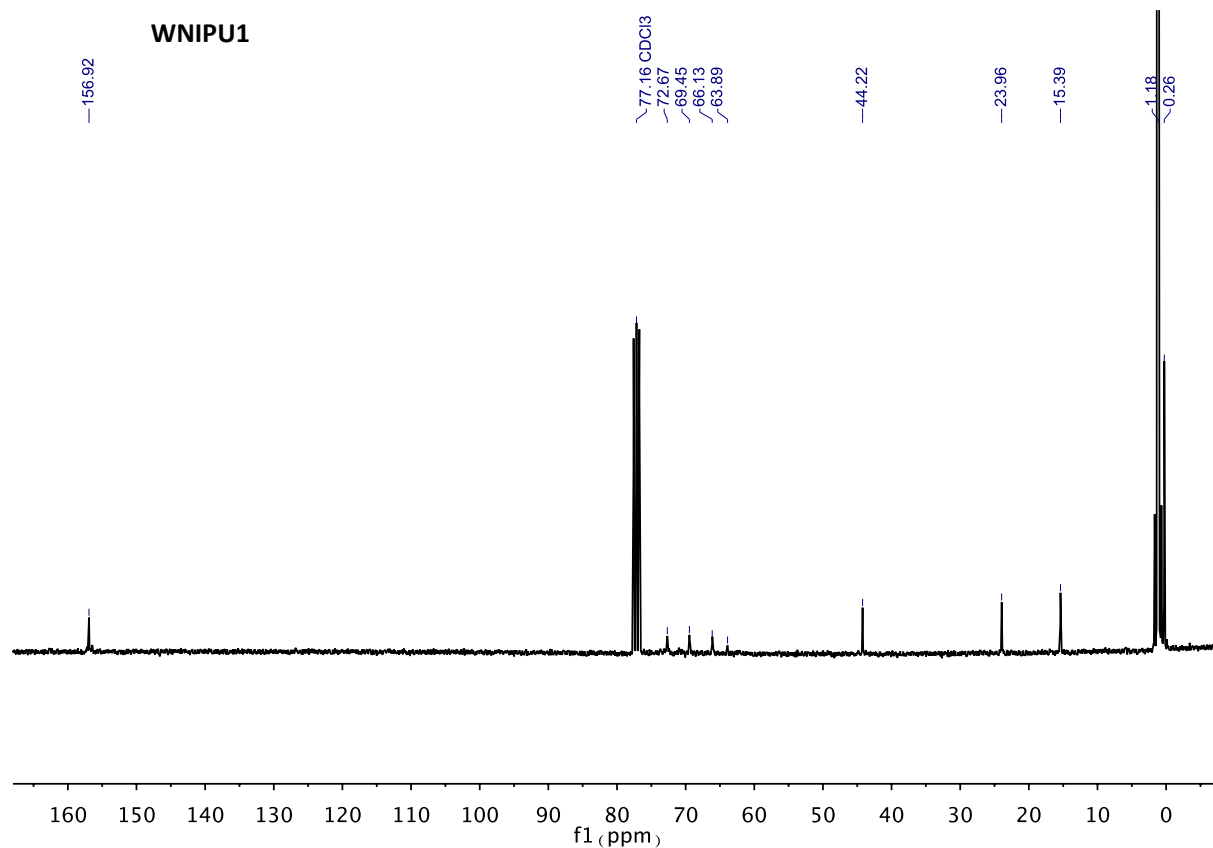


Figure S3. ¹³C NMR of WNIPU1 (100-0 ratio), (75 MHz, CDCl₃) δ (ppm) = 156.9 (–NH–(C=O)–O–), 72.7, 69.4, 66.1, 63.9 (CH₂O and CHO), 44.2 (CH₂NH), 23.9 (CH₂), 15.4 (SiCH₂), 1.2, 0.26 (SiCH₃).

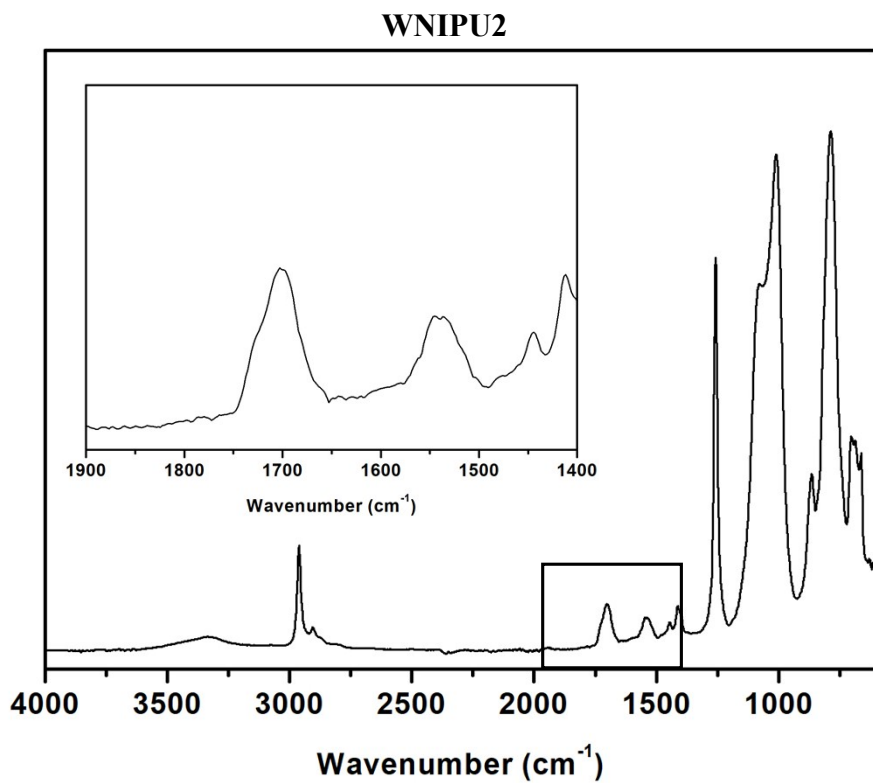


Figure S4. FTIR spectrum of WNIPU2.

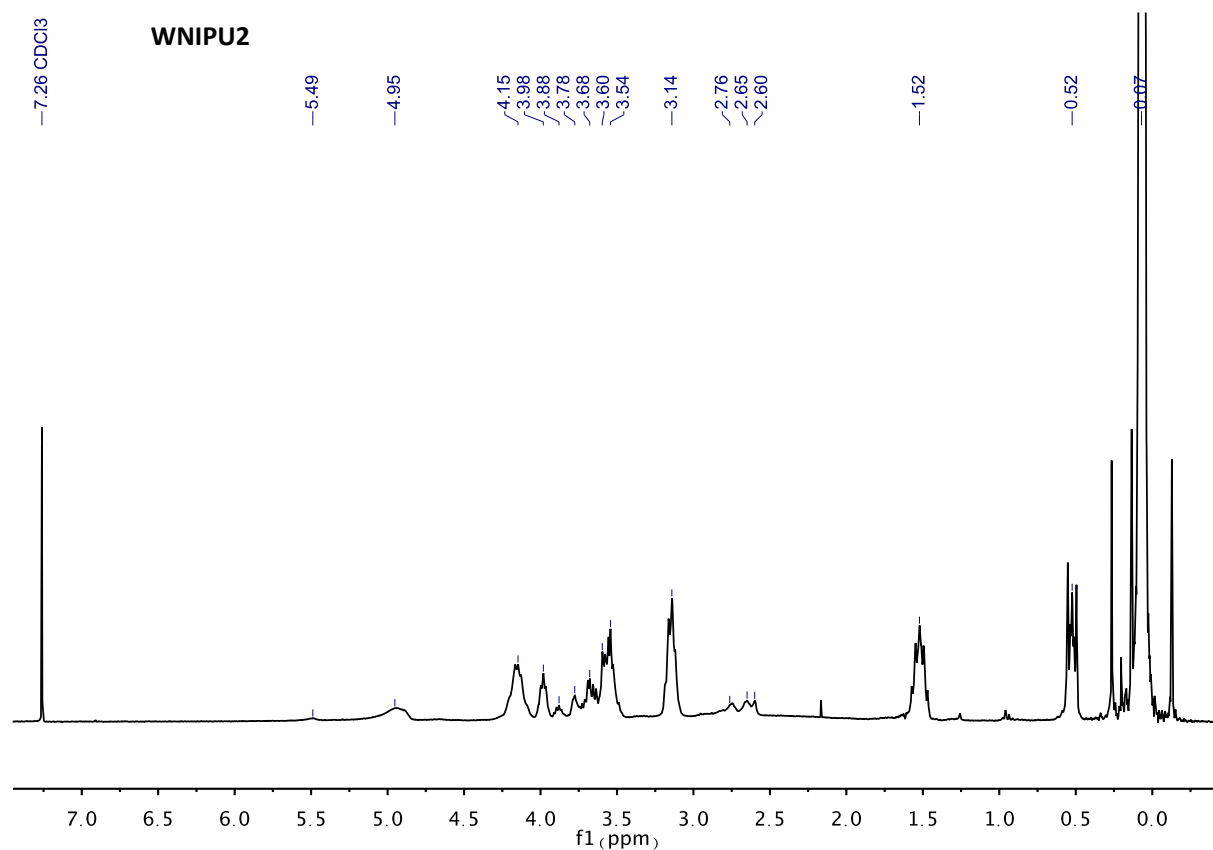


Figure S5. ^1H NMR of WNIPU2 (90-10 ratio), (300 MHz, CDCl_3) δ (ppm) = 5.49 (s, CHOH), 4.95 (bs, $\text{CHO}(\text{CO})\text{N}$), 4.15 (m, $\text{CH}_2\text{O}(\text{CO})\text{N}$), 3.98 (m, CHCH_2O), 3.88 (m,

CHOH), 3.78 (m, CH₂CHCH₂O), 3.68-3.54 (m, CH₂OH), 3.14 (q, CH₂NH), 2.76-2.60 (m, CH₂N), 1.52 (quintuplet, SiCH₂CH₂CH₂NH), 0.52 (t, SiCH₂), 0.07 (s, SiCH₃).

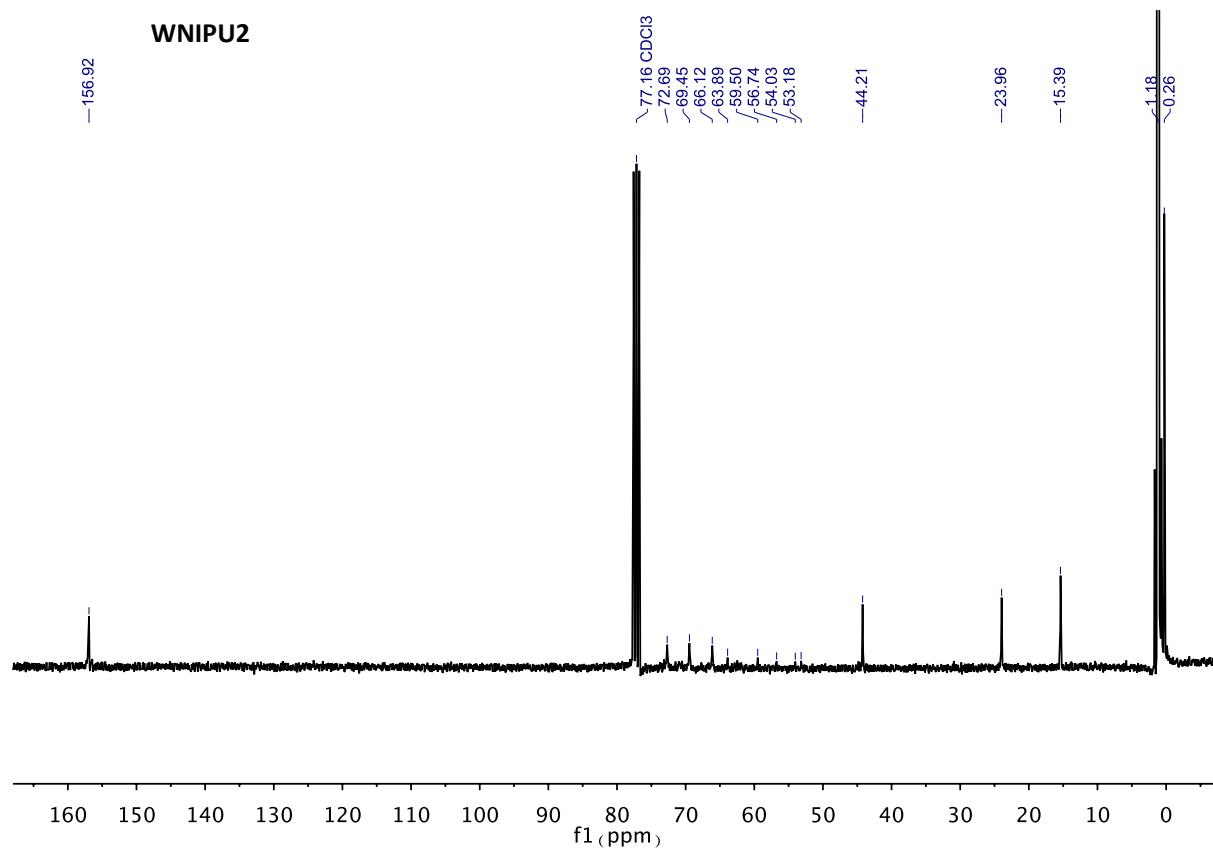


Figure S6. ¹³C NMR of WNIPU2 (90-10 ratio), (75 MHz, CDCl₃) δ (ppm) = 156.9 (–NH–(C=O)–O–), 72.7, 69.4, 66.1, 63.9, 59.5, 56.7, 54.0, 53.2 (CH₂O, CHO and CH₂N), 44.2 (CH₂NH), 23.9 (CH₂), 15.4 (SiCH₂), 1.2, 0.26 (SiCH₃).

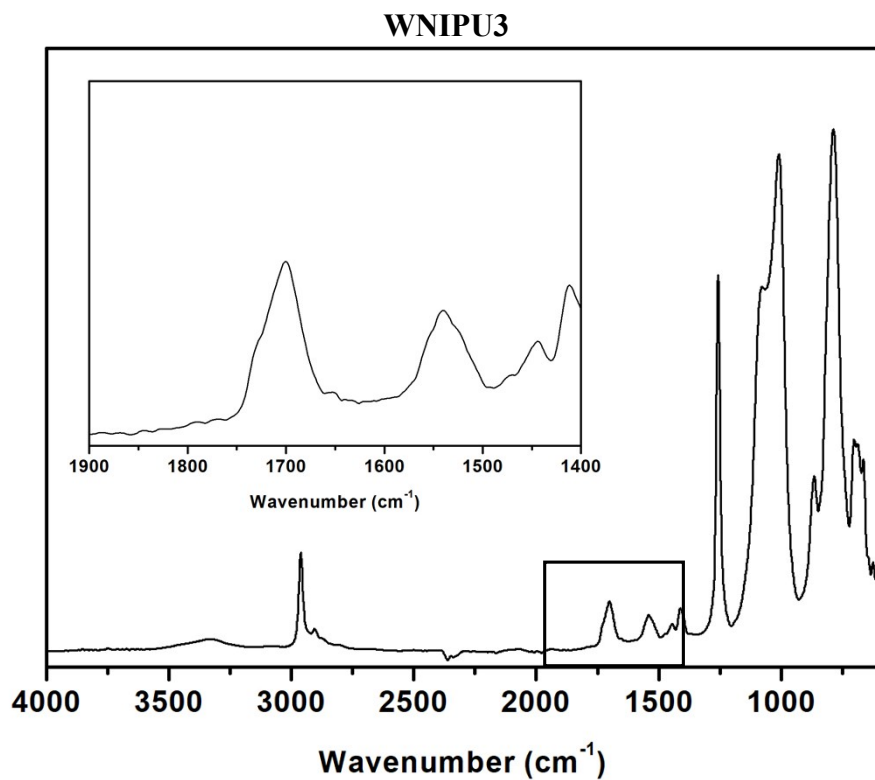


Figure S7. FTIR spectrum of WNIPU3.

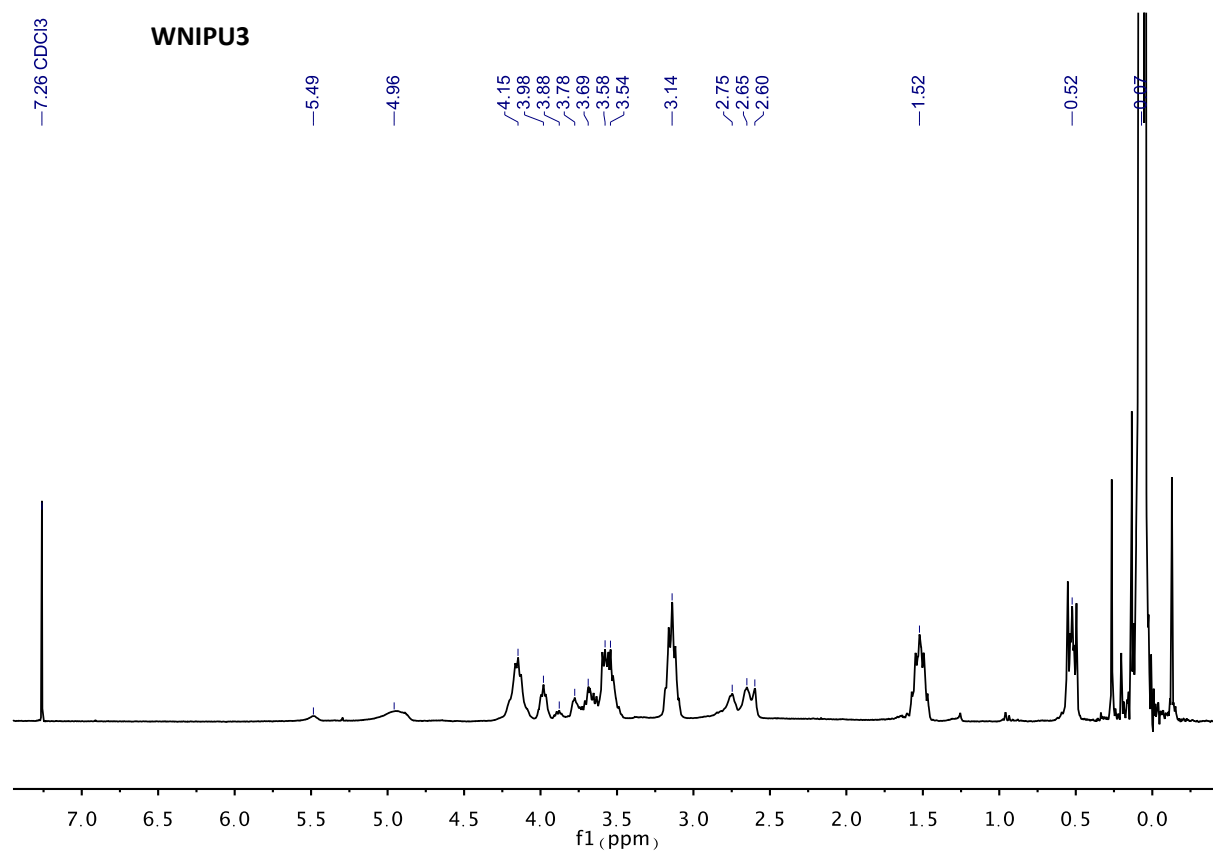


Figure S8. ^1H NMR of WNIPU3 (80-20 ratio), (300 MHz, CDCl_3) δ (ppm) = 5.49 (s, CHOH), 4.96 (bs, $\text{CHO}(\text{CO})\text{N}$), 4.15 (m, $\text{CH}_2\text{O}(\text{CO})\text{N}$), 3.98 (m, CHCH_2O), 3.88 (m,

CHOH), 3.78 (m, CH₂CHCH₂O), 3.69-3.54 (m, CH₂OH), 3.14 (q, CH₂NH), 2.75-2.60 (m, CH₂N), 1.52 (quintuplet, SiCH₂CH₂CH₂NH), 0.52 (t, SiCH₂), 0.07 (s, SiCH₃).

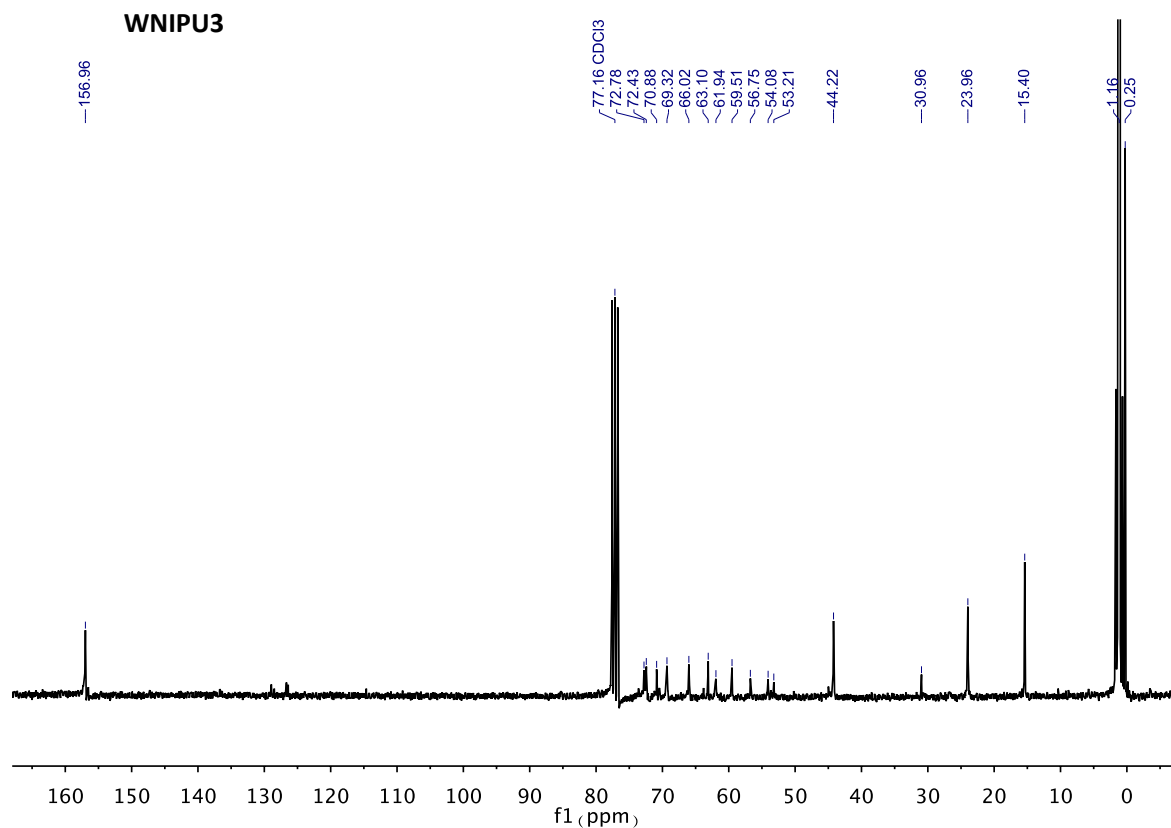


Figure S9. ¹³C NMR of WNIPU3 (80-20 ratio), (75 MHz, CDCl₃) δ (ppm) = 156.9 (–NH–(C=O)–O–), 72.8, 72.4, 70.1, 69.3, 66.0, 63.1, 61.9, 59.5, 56.7, 54.0, 53.2 (CH₂O, CHO and CH₂N), 44.2 (CH₂NH), 30.9, 23.9 (CH₂), 15.4 (SiCH₂), 1.2, 0.25 (SiCH₃).

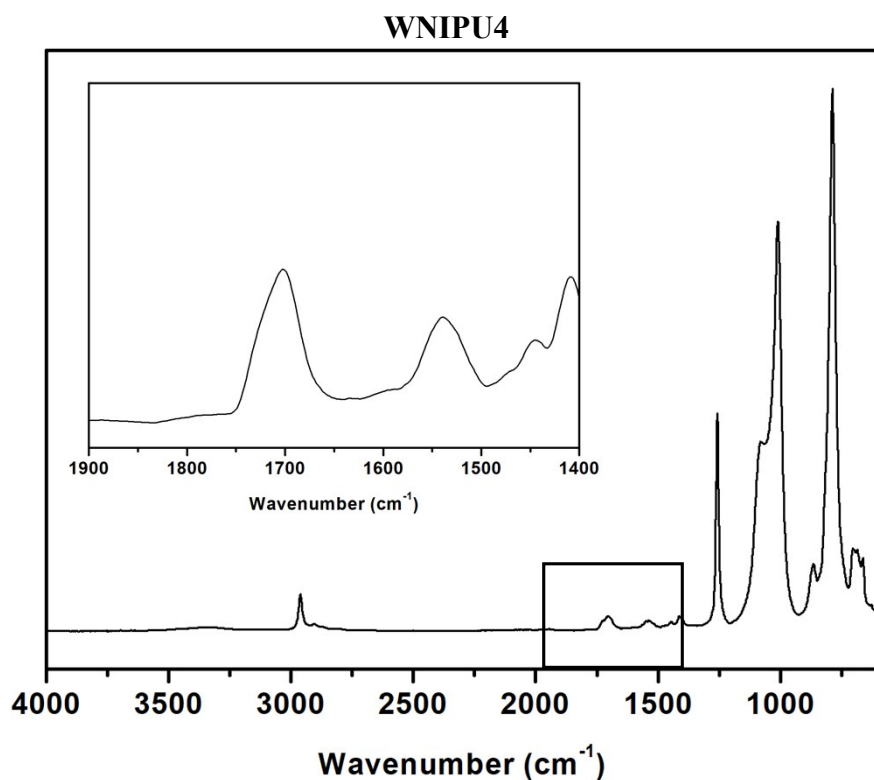


Figure S10. FTIR spectrum of WNIPU4.

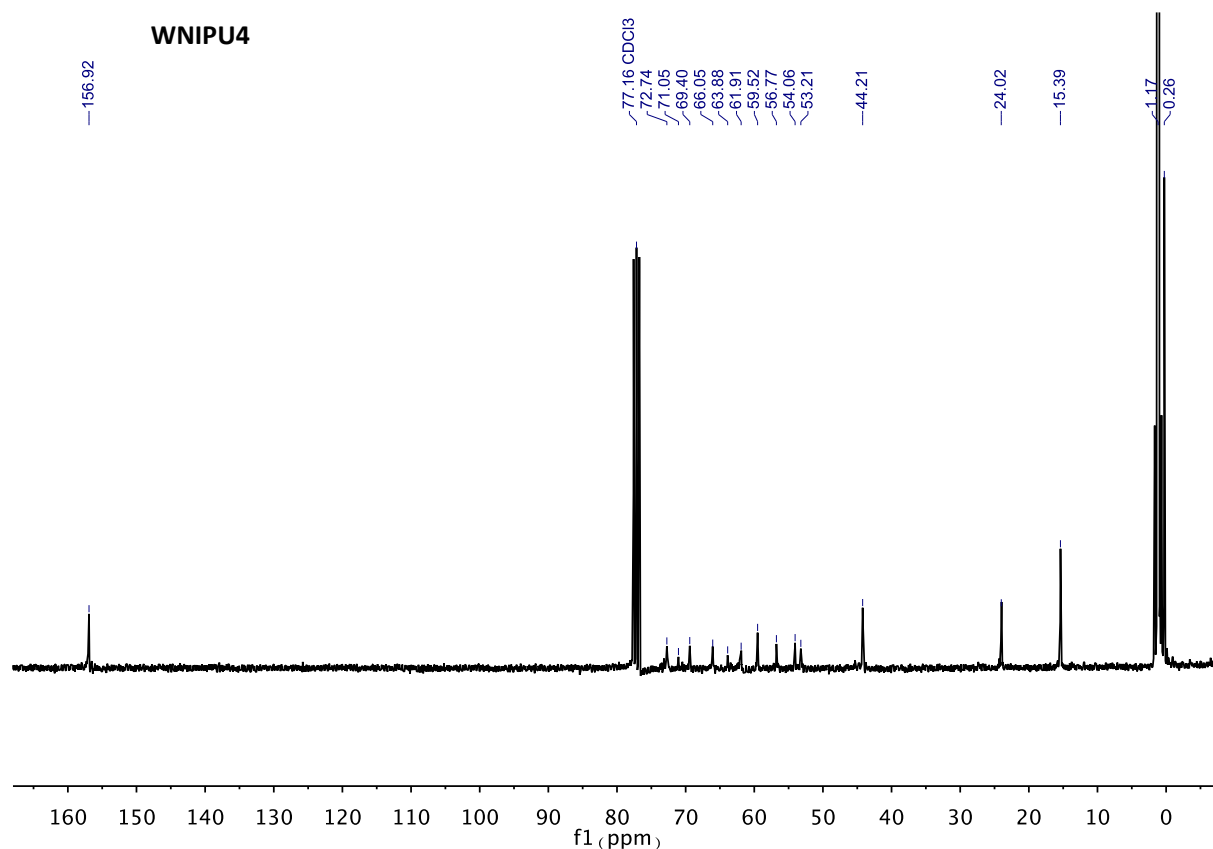


Figure S11. ¹³C NMR of WNIPU4 (70-30 ratio), (75 MHz, CDCl₃) δ (ppm) = 156.9 (–NH–(C=O)–O–), 72.7, 71.0, 69.4, 66.1, 63.9, 61.9, 59.5, 56.7, 54.0, 53.2 (CH₂O, CHO and CH₂N), 44.2 (CH₂NH), 24.0 (CH₂), 15.4 (SiCH₂), 1.2, 0.26 (SiCH₃).

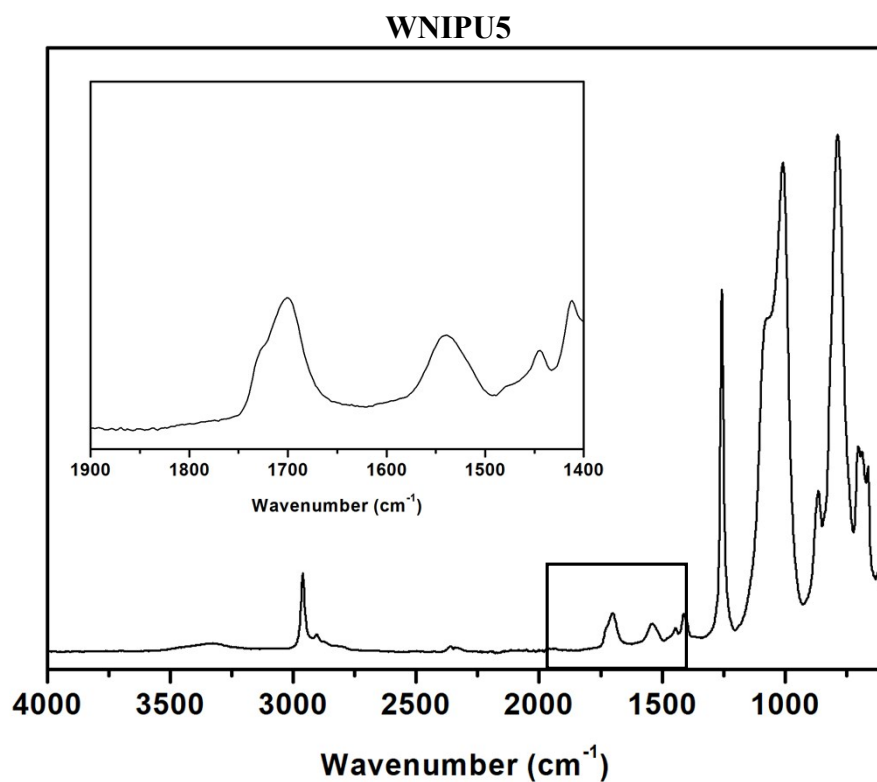


Figure S12. FTIR spectrum of WNIPU5.

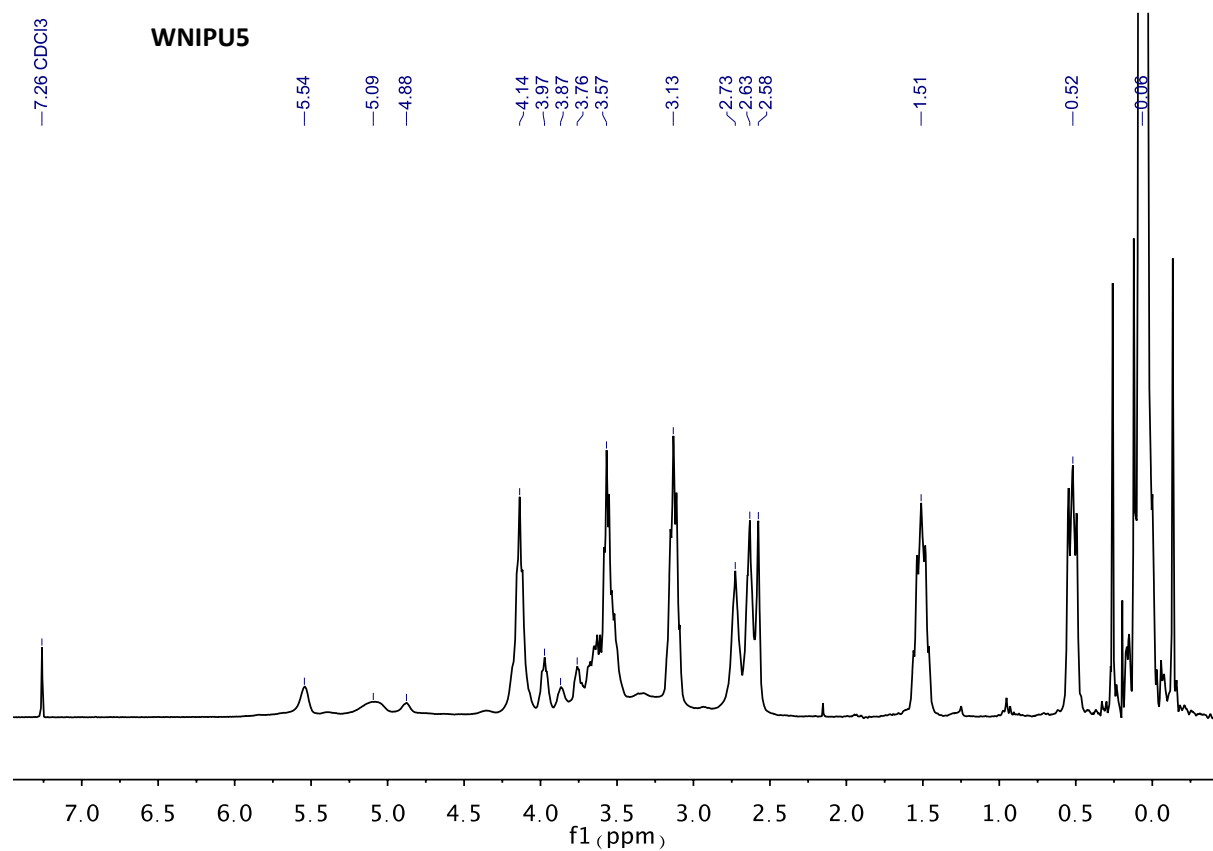


Figure S13. ^1H NMR of WNIPU5 (60-40 ratio), (300 MHz, CDCl_3) δ (ppm) = 5.54 (s, CHOH), 5.09 (bs, CHOH), 4.88 (bs, $\text{CHO}(\text{CO})\text{N}$), 4.14 (m, $\text{CH}_2\text{O}(\text{CO})\text{N}$), 3.97 (m, CHCH_2O), 3.87 (m, CHOH), 3.76 (m, $\text{CH}_2\text{CHCH}_2\text{O}$), 3.68-3.55 (m, CH_2OH), 3.13 (q,

CH_2NH), 2.73-2.58 (m, CH_2N), 1.51 (quintuplet, $SiCH_2CH_2CH_2NH$), 0.52 (t, $SiCH_2$), 0.06 (s, $SiCH_3$).

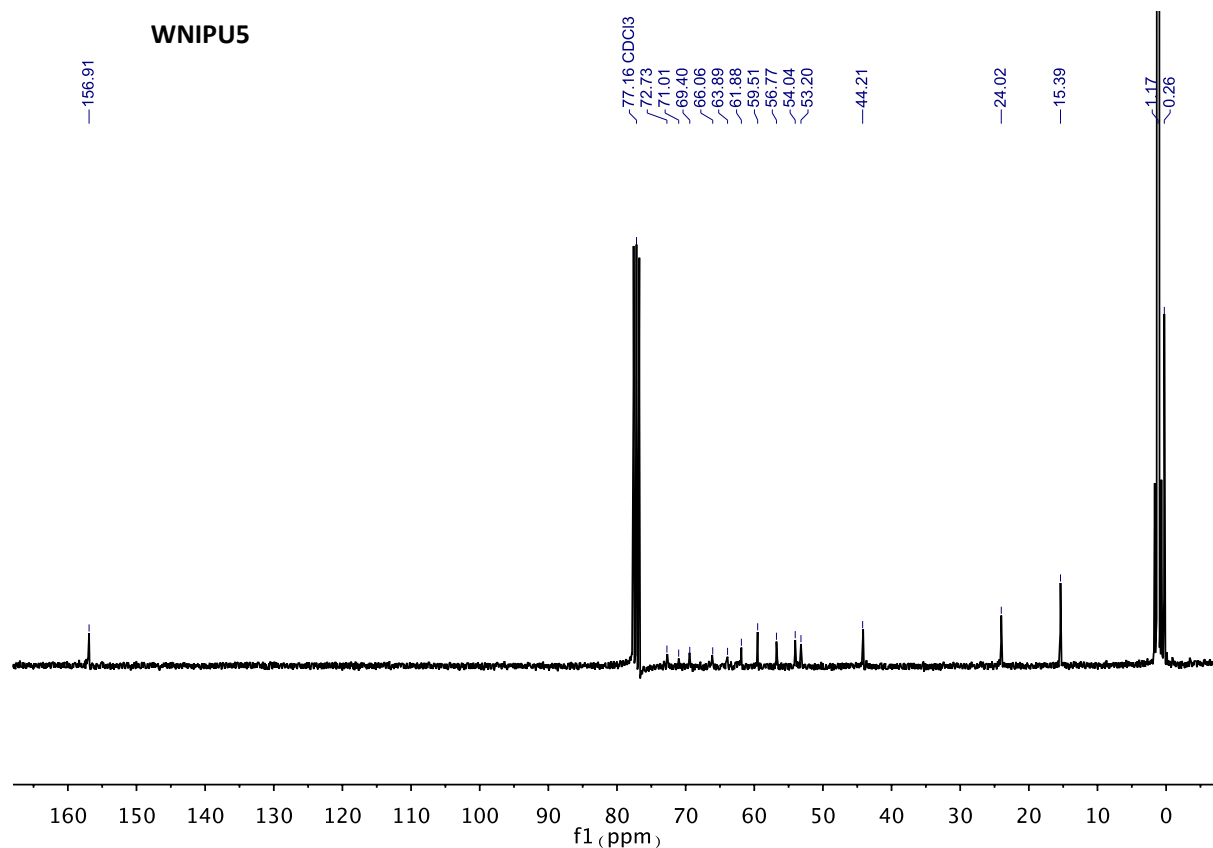


Figure S14. ^{13}C NMR of WNIPU5 (60-40 ratio), (75 MHz, $CDCl_3$) δ (ppm) = 156.9 ($-NH-(C=O)-O-$), 72.7, 71.0, 69.4, 66.1, 63.9, 61.9, 59.5, 56.7, 54.0, 53.2 (CH_2O , CHO and CH_2N), 44.2 (CH_2NH), 24.0 (CH_2), 15.4 ($SiCH_2$), 1.2, 0.26 ($SiCH_3$).

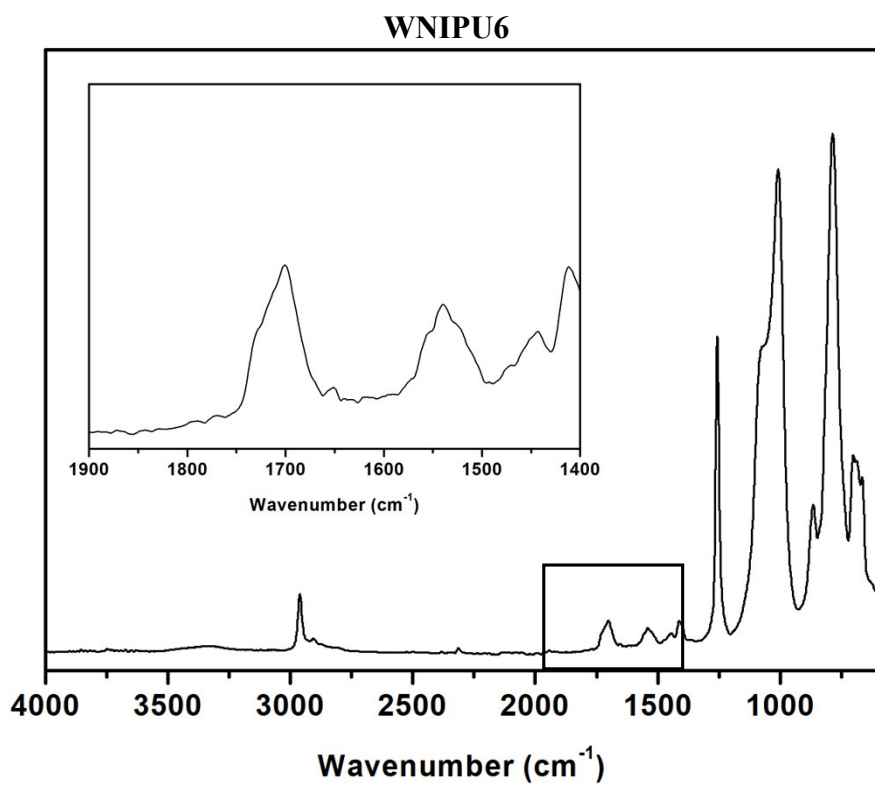


Figure S15. FTIR spectrum of WNIPU6.

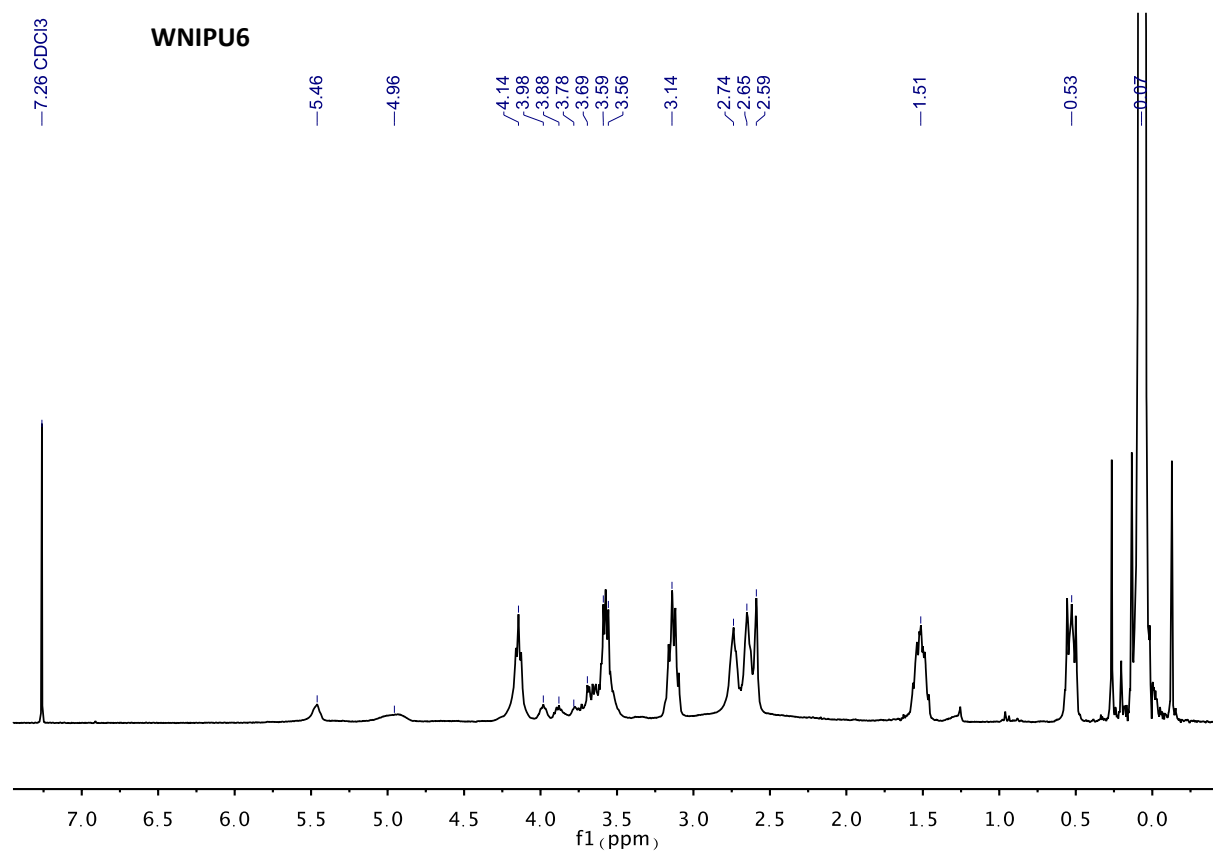


Figure S16. ^1H NMR of WNIPU6 (50-50 ratio), (300 MHz, CDCl_3) δ (ppm) = 5.49 (s, CHOH), 4.96 (bs, $\text{CHO}(\text{CO})\text{N}$), 4.14 (m, $\text{CH}_2\text{O}(\text{CO})\text{N}$), 3.98 (m, CHCH_2O), 3.88 (m,

CHOH), 3.78 (m, CH₂CHCH₂O), 3.69-3.56 (m, CH₂OH), 3.14 (q, CH₂NH), 2.74-2.59 (m, CH₂N), 1.51 (quintuplet, SiCH₂CH₂CH₂NH), 0.53 (t, SiCH₂), 0.07 (s, SiCH₃).

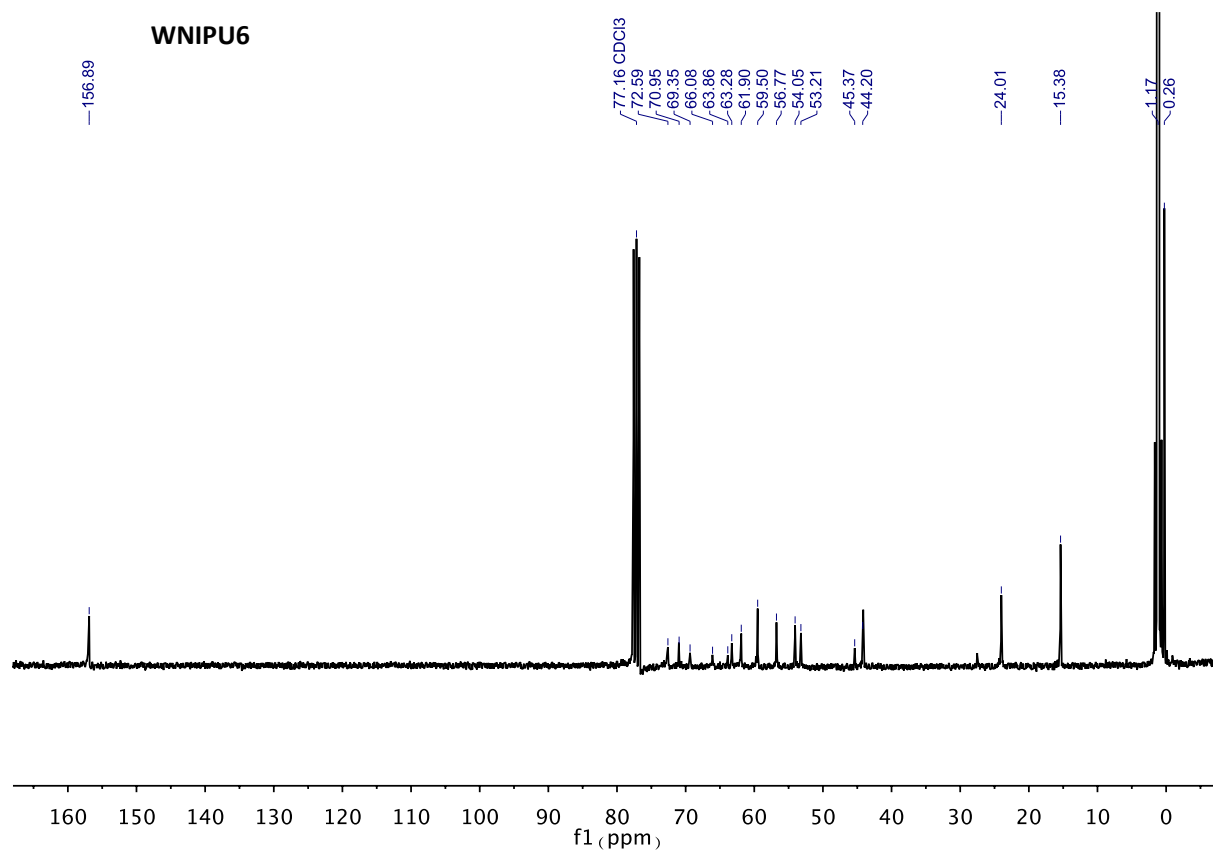


Figure S17. ¹³C NMR of WNIPU6 (50-50 ratio), (75 MHz, CDCl₃) δ (ppm) = 156.9 (–NH–(C=O)–O–), 72.6, 70.1, 69.3, 66.1, 63.3, 61.9, 59.5, 56.8, 54.0, 53.2 (CH₂O, CHO and CH₂N), 45.4, 44.2 (CH₂NH), 24.0 (CH₂), 15.4 (SiCH₂), 1.2, 0.26 (SiCH₃).

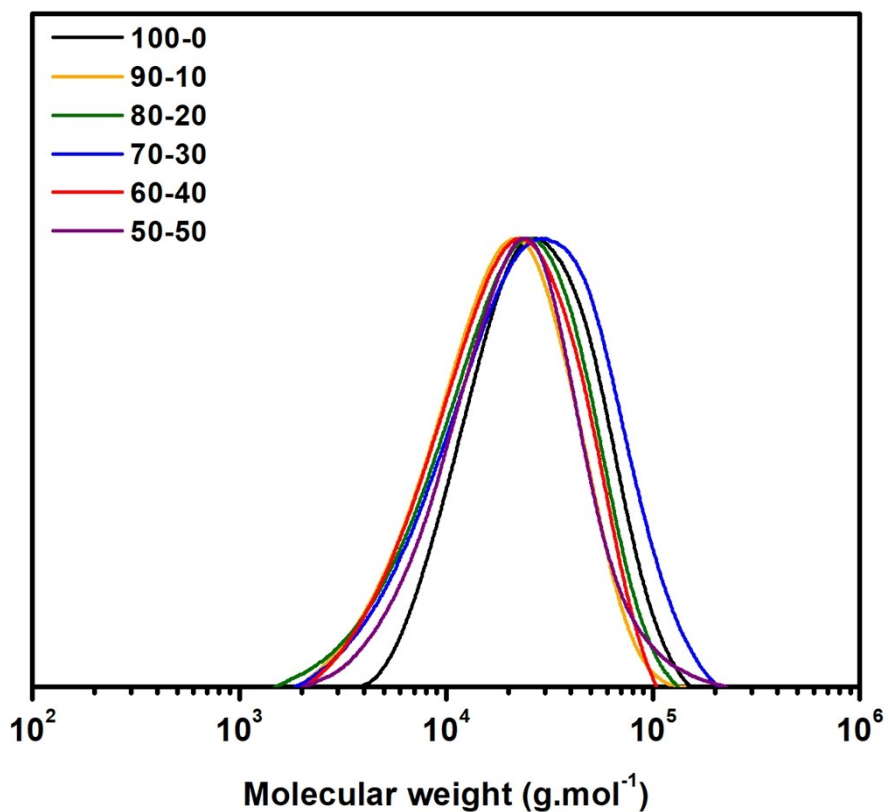


Figure S18. SEC chromatograms of the synthesized poly(hydroxyurethanes).

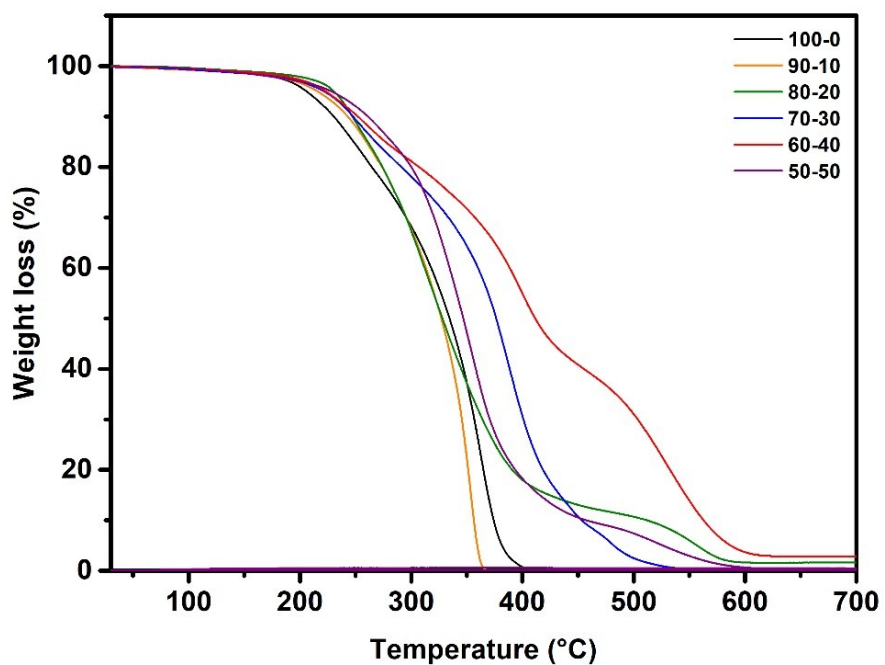


Figure S19. TGA thermograms of the synthesized poly(hydroxyurethanes).

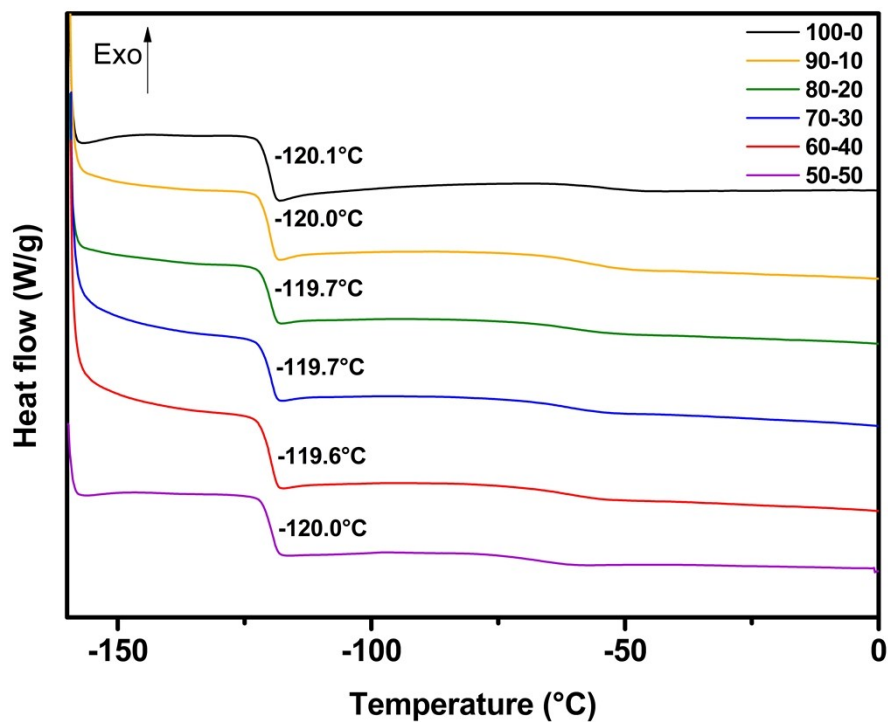


Figure S20. DSC curves of the synthesized poly(hydroxyurethanes).

Experimental S1. Influence of the initial solid content.

It is known that the initial PU content is a criterion that can have an important impact on the phase-inversion process and thus on the final particle size. To study this parameter in our WNIPU system, dispersion experiments were carried out varying the initial PHU contents, *i.e.* 40, 50 and 60 wt %, using WNIPU4 and excess acetic acid to ensure full neutralization. As can be seen in **Table S1**, lower initial solid content in the dispersion led to slightly larger particle sizes with broader dispersity before removal of acetone. However, once the acetone was removed and on the range of initial solid content studied, no significant differences on the particle sizes could be observe; although one can notice that the dispersion produced with an initial solid content of 60 wt % was more reproducible as characterized by a low standard deviation. The average particle size was essentially constant at 200 nm. In our opinion, this behavior can be explained considering that in the acetone process, the polymer particles are formed early in the phase inversion process, as water addition promotes the restructure of the polymer-water interface. At this point the number of particles is fixed. Further addition of water is just a dilution process.

Table S1. Influence of the initial solid content.

Initial solid content (wt %) ^a	$D_{pwater/acetone}$ (nm) ^b	PDI ^b	D_{pwater} (nm) ^c	PDI ^c
40	267 (± 31)	0.27 (± 0.2)	201 (± 25)	0.31 (± 0.2)
50	189 (± 16)	0.15 (± 0.02)	196 (± 23)	0.16 (± 0.01)
60	193 (± 5)	0.27 (± 0.06)	210 (± 4)	0.14 (± 0.02)

^aBased on the total mass of polymer and acetone. ^bParticle sizes and particle size distributions were calculated using DLS in water/acetone mixture over 3 experiments. ^cParticle sizes and particle size distributions were calculated using DLS after acetone removal over 3 experiments. Dispersion experiments were carried out at room temperature from WNIPU4 and a degree of neutralization of 100 %.



Figure S21. Photographs of the dispersion obtained from WNIPU3 after acetone removal (left) and WNIPU4 one year after



Figure S22. Photograph of the film obtained incorporating 100 mol % of citric acid into the WNIPU4 dispersion after immersion in water.

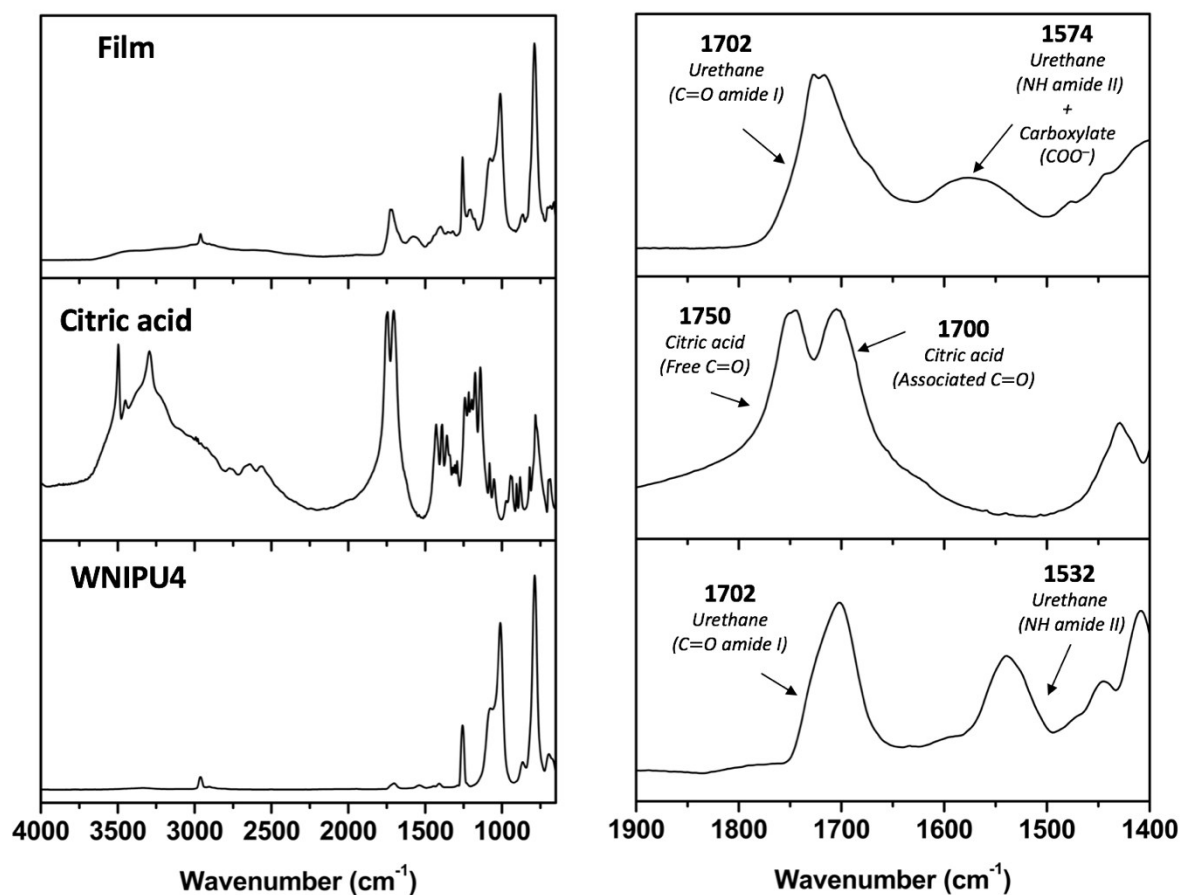


Figure S23. FTIR spectra of citric acid, WNIPU4 and WNIPU4/citric acid film.

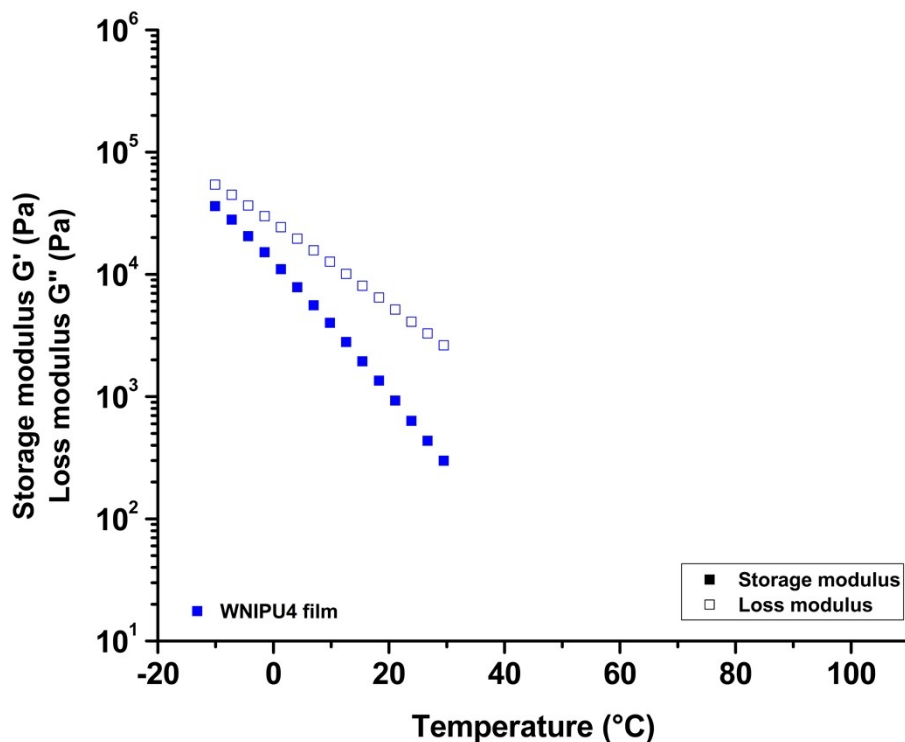


Figure S24. Evolution of the storage and loss modulus (G' and G'') as a function of temperature for the film prepared from WNIPU4 dispersion.

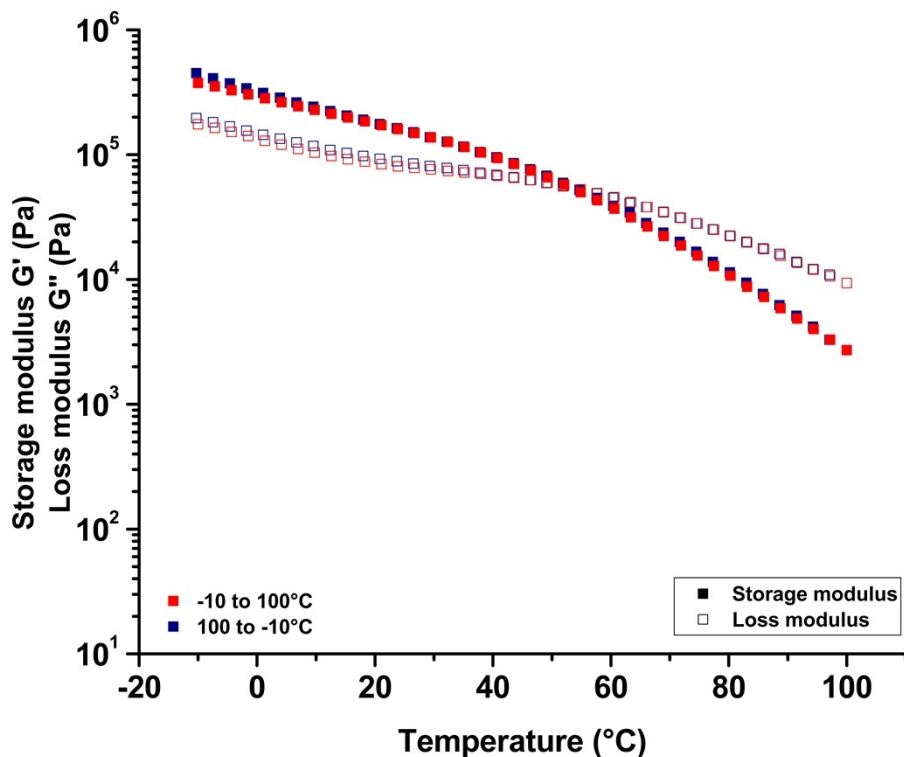


Figure S25. Evolution of the storage and loss modulus (G' and G'') in reverse temperature sweep between -10 and 100°C for the WNIPU4/citric acid film.

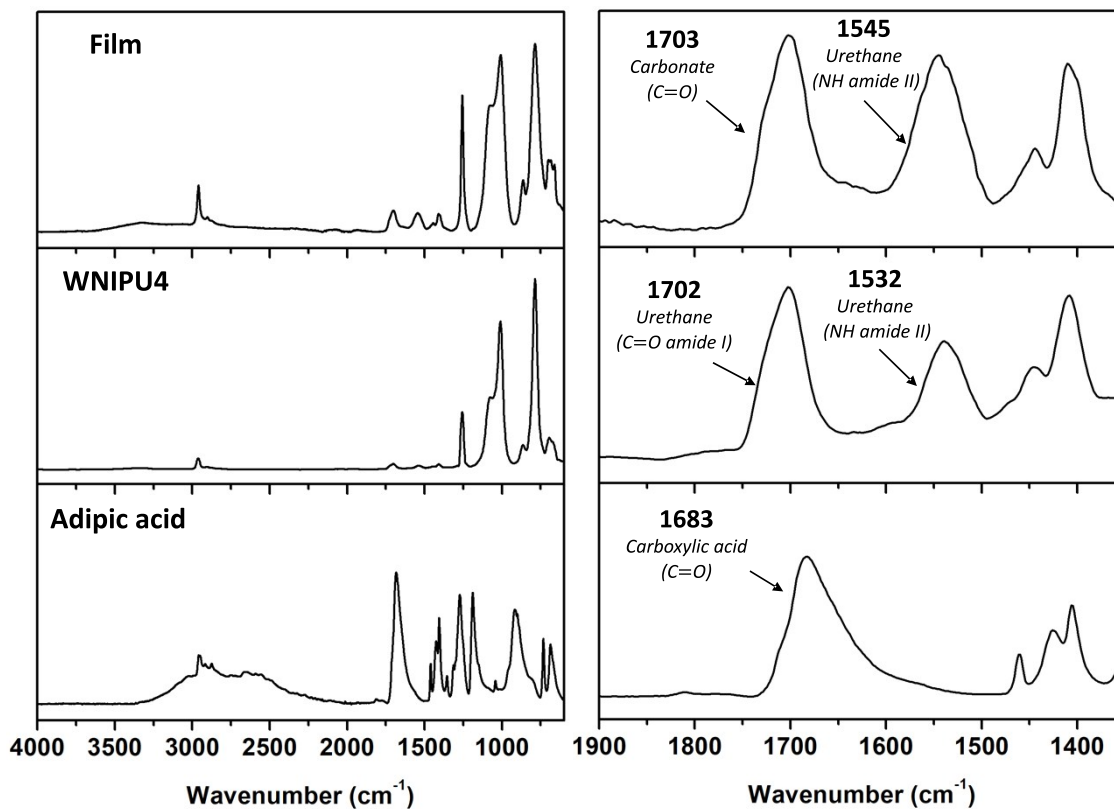


Figure S26. FTIR spectra of adipic acid, WNIPU4 and WNIPU4/adipic acid film.

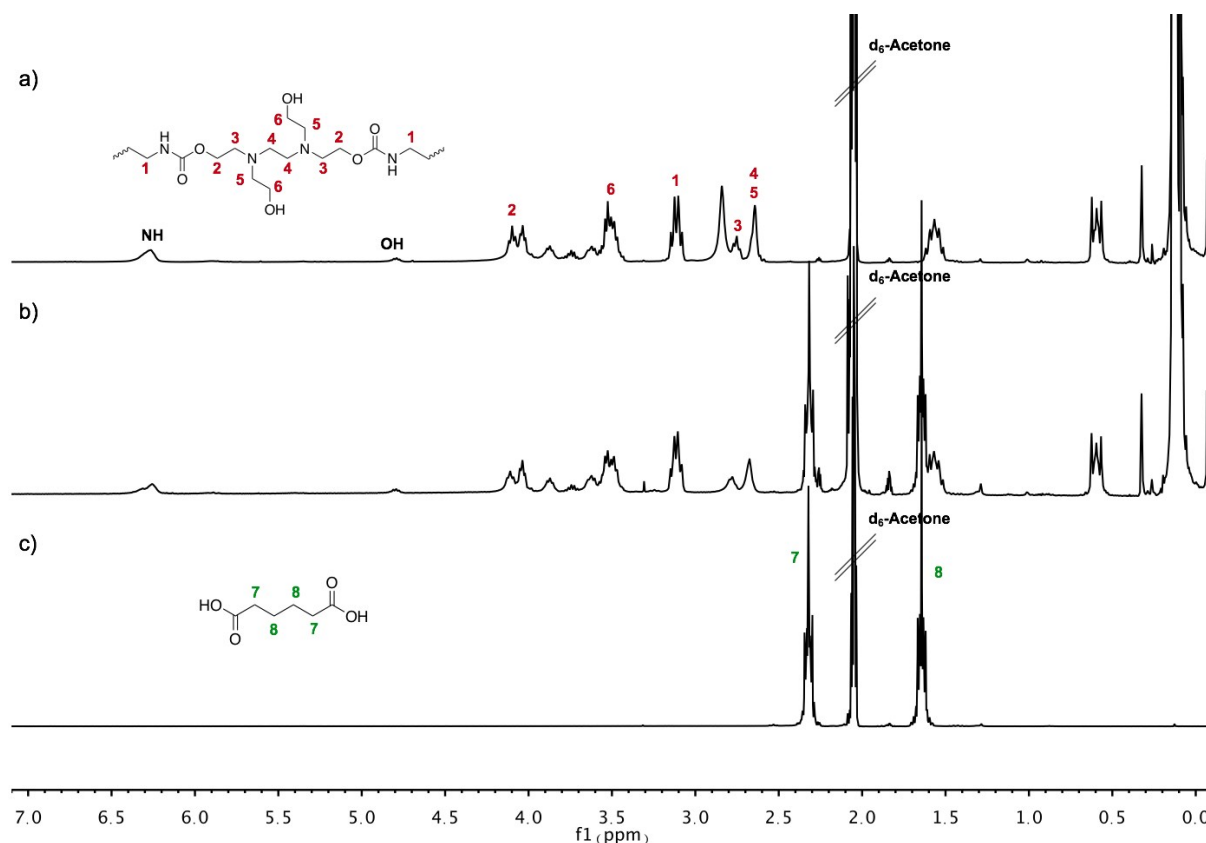


Figure S27. ^1H NMR (300 MHz, d_6 -acetone) of a) WNIPU4, b) WNIPU4/adipic acid film and c) adipic acid showing no proton shift associated with the formation of ionic bonds.

Experimental S2. Preparation of covalently crosslinked films

The films were prepared using the poly(hydroxyurethane) composed of 70 mol. % of DGC and 30 mol. % of bis-N-8-C. First, 1 g of polymer was dissolved in 2 mL of acetone. Then, 80 μL of divinyl sulfone curing agent (excess) was added. The mixture was kept under stirring for 1 h at room temperature. The films were casted on a microscope slide and dried at room temperature for 24 h and 3 days at 80 $^\circ\text{C}$ under vacuum

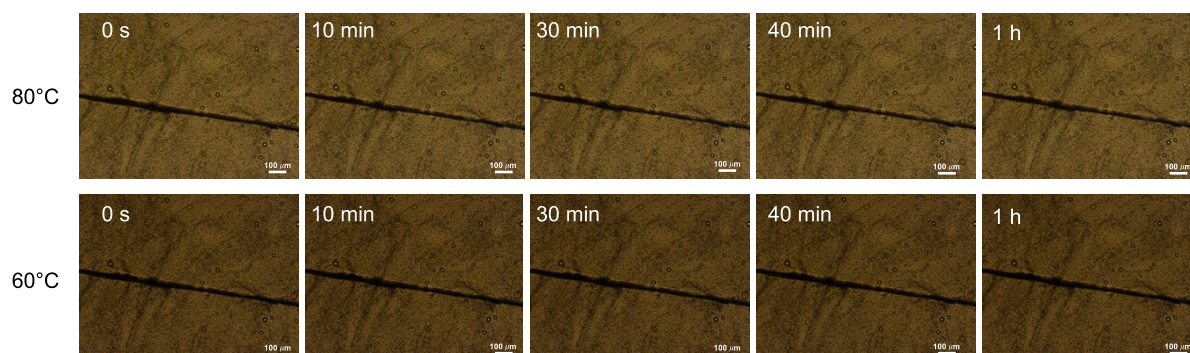


Figure S28. Evolution of the crack refilling process at different temperatures for covalently crosslinked films prepared from the poly(hydroxyurethane) composed of 70 mol. % of DGC and 30 mol. % of bis-N-8-C and excess divinyl sulfone.