Supporting Information

Turn things around: from cationic/anionic complexation-induced nanoemulsion instability to toughen water resistant waterborne polyurethanes

*Yuan Yao, Meng Xiao, and Wenguang Liu**

Y. Yao, Prof. W. Liu.
School of Materials Science and Engineering
Tianjin Key Laboratory of Composite and Functional Materials
Tianjin University
Tianjin 300350, China
E-mail: wgliu@tju.edu.cn

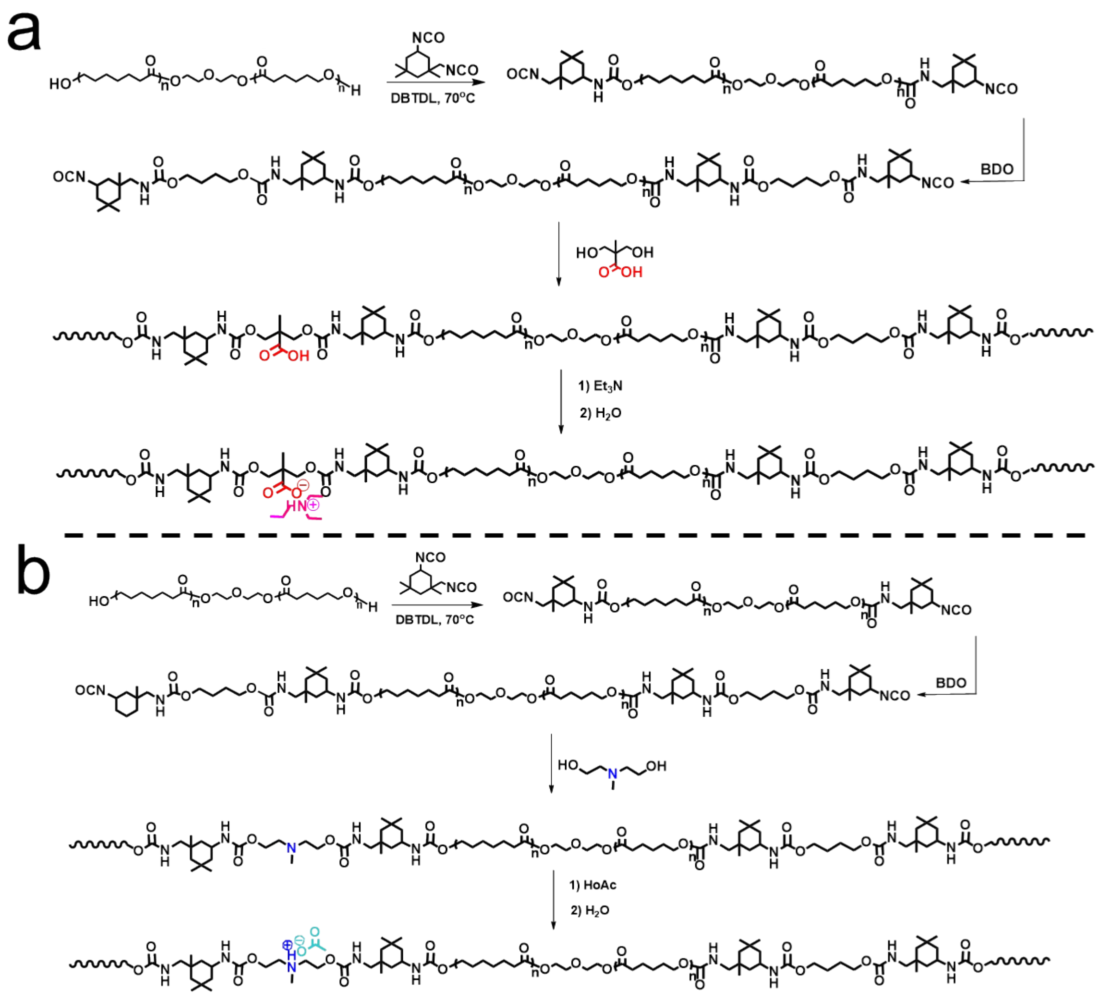

Figure S1. Synthesis and chemical structures of supramolecular (a) WPU- and (b) WPU+ elastomer.

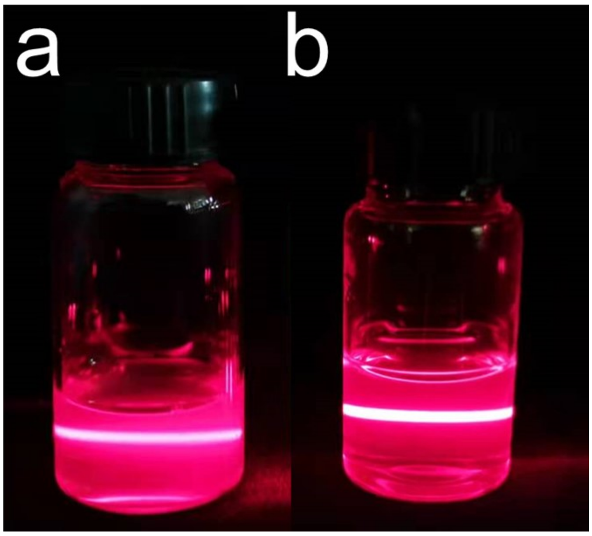

Figure S2. Tyndall effect of laser beam scattering with a) WPU+ and b) WPU- dispersions, showing colloidal particle formation in water.

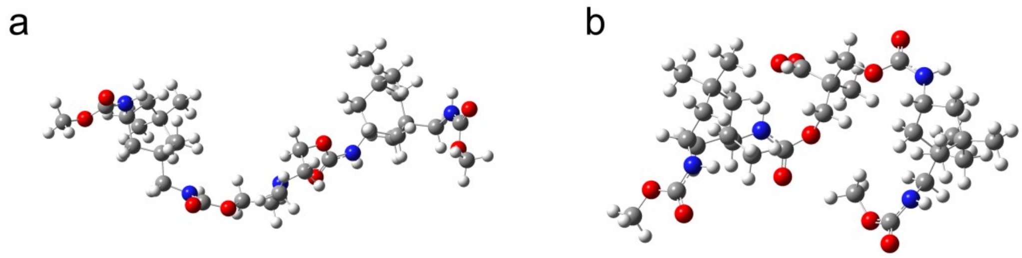

Figure S3. Conformation of hydrophilic hard segments in model system: (a) WPU+; (b) WPU-.

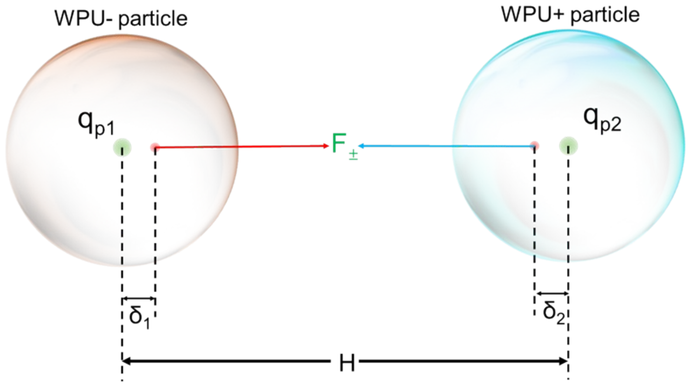

Figure S4. Model of electrostatic attraction of oppositely charged particles.

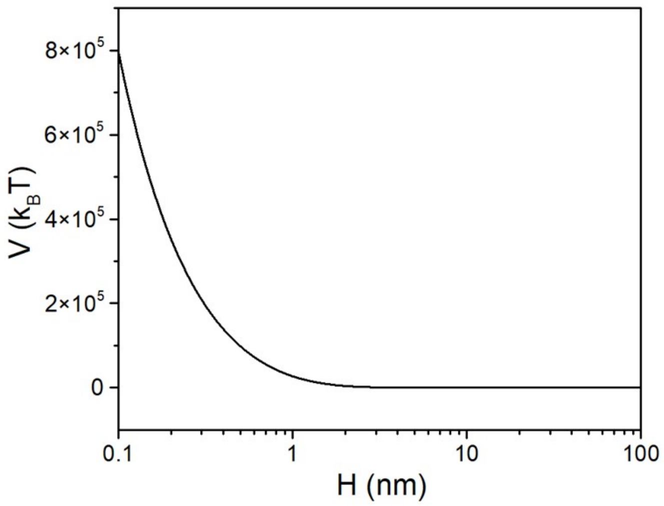

Figure S5. Plot of the electrostatic attraction potential energy for two oppositely charged particles separated by a distance H.

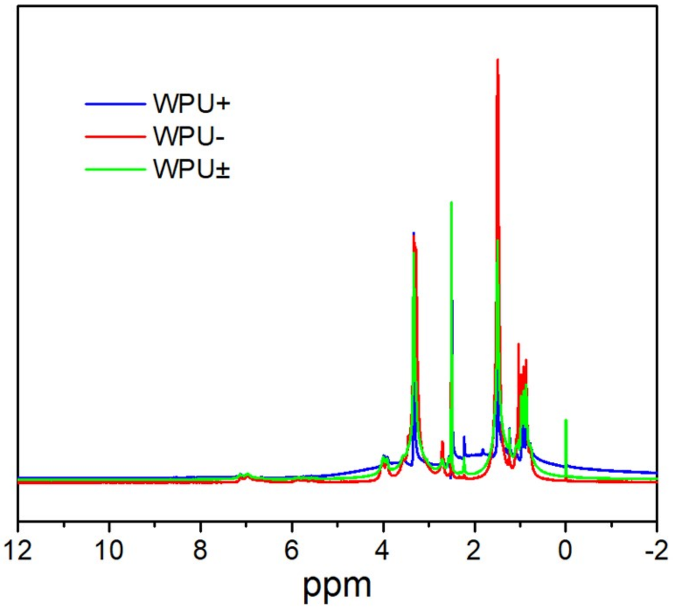

Figure S6. ^{1}H NMR spectra of WPU polymers in DMSO-d6. The spectrum indicated that there were typical characteristic peaks of the carbamate (7.00 ppm attributed to -NH-), and PCL diol (2.23, 1.50, and 4.00 ppm attributed to methylene).

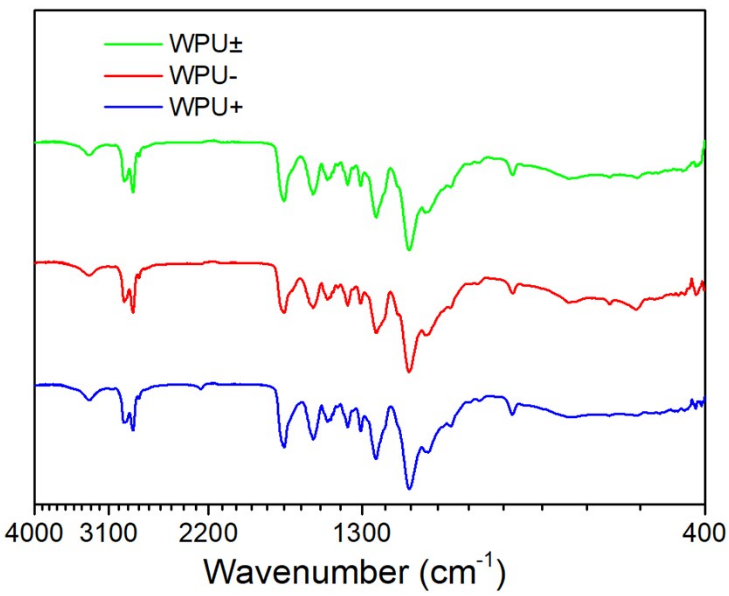

Figure S7. FTIR spectra of WPU films.

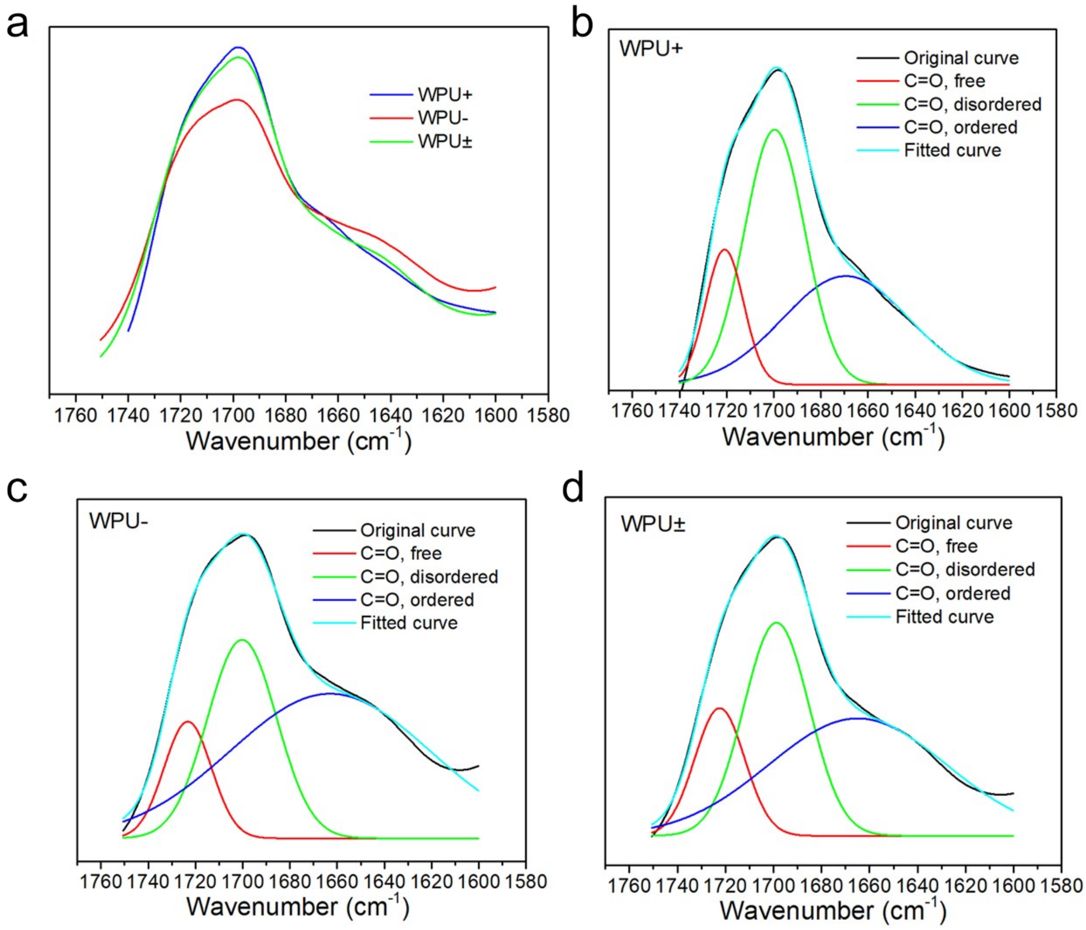

Figure S8. a) FTIR Spectra of WPUs in the range from 1600 to 1750 cm^{-1}. Splits of stretching vibration C=O bands in the FTIR spectra of b) WPU+, c) WPU- and d) WPU± via peak deconvolution method.

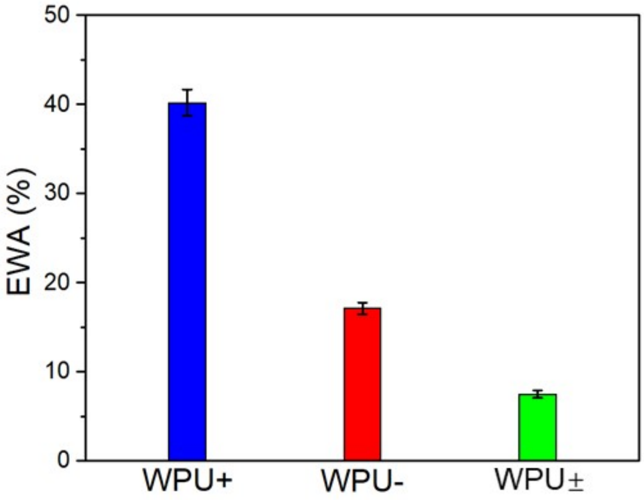

Figure S9. Equilibrium water absorptions of WPUs. (n=3)

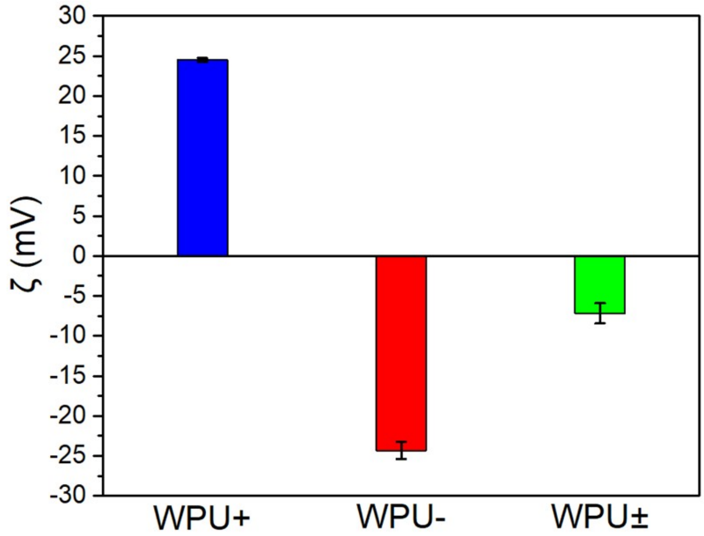

Figure S10. Surface zeta potentials of WPUs. (n=3)

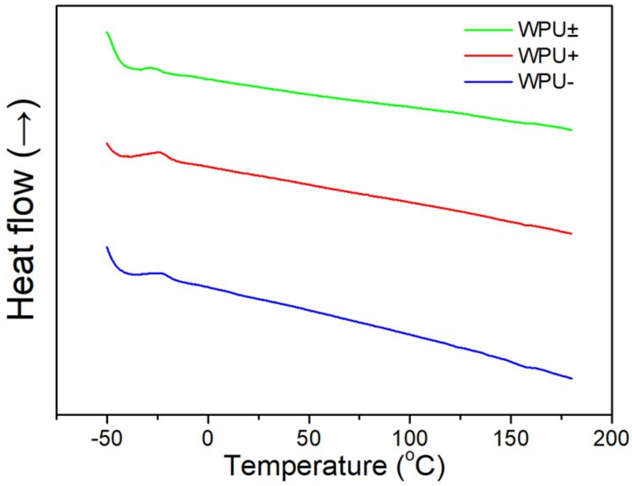

Figure S11. DSC curves of WPUs.

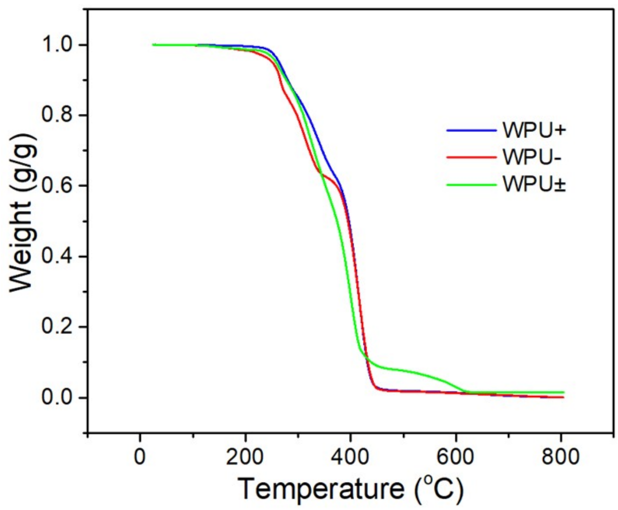

Figure S12. TGA curves of WPUs.

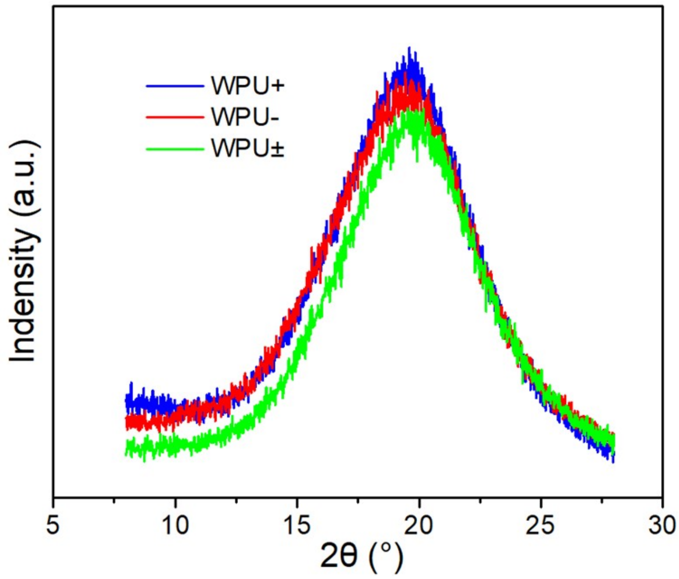

Figure S13. XRD patterns of WPUs.

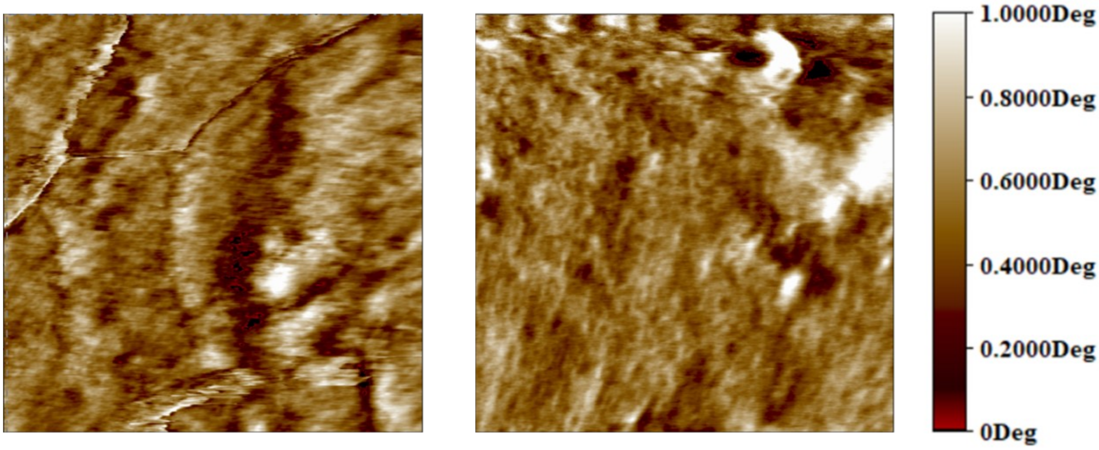

Figure S14. AFM images of WPU+ film (left) and WPU- film (right). Size 1 μm×1 μm.

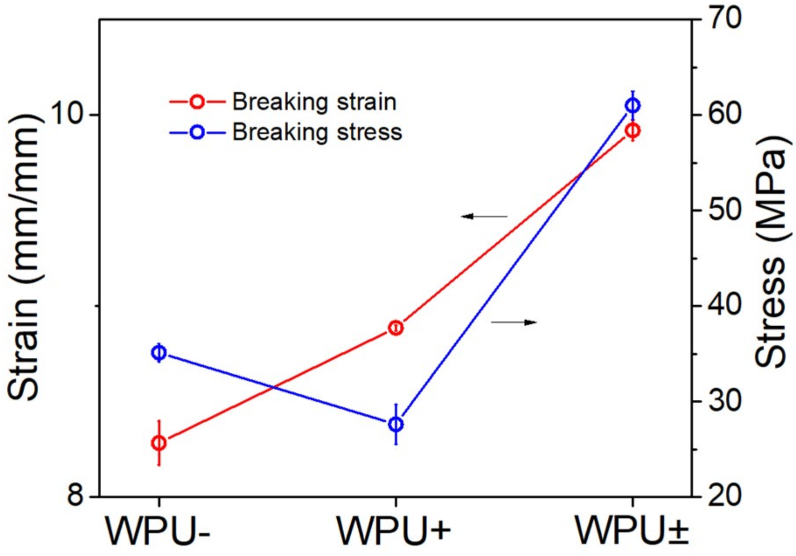

Figure S15. Breaking strain and tensile strength of WPUs.

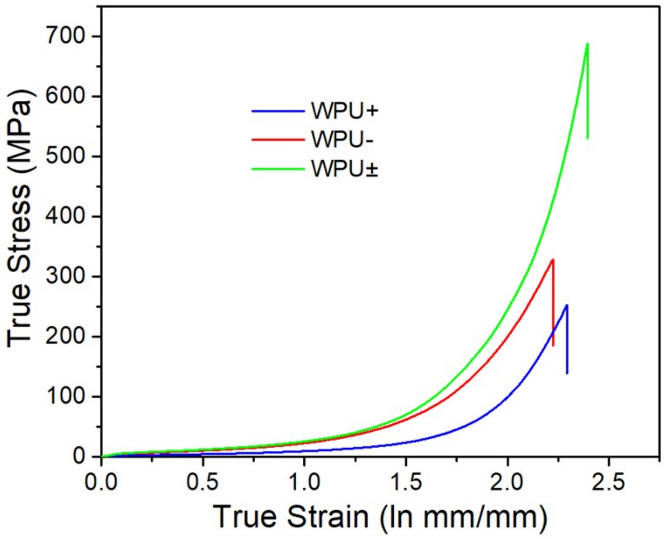

Figure S16. True stress–strain curves of WPUs.

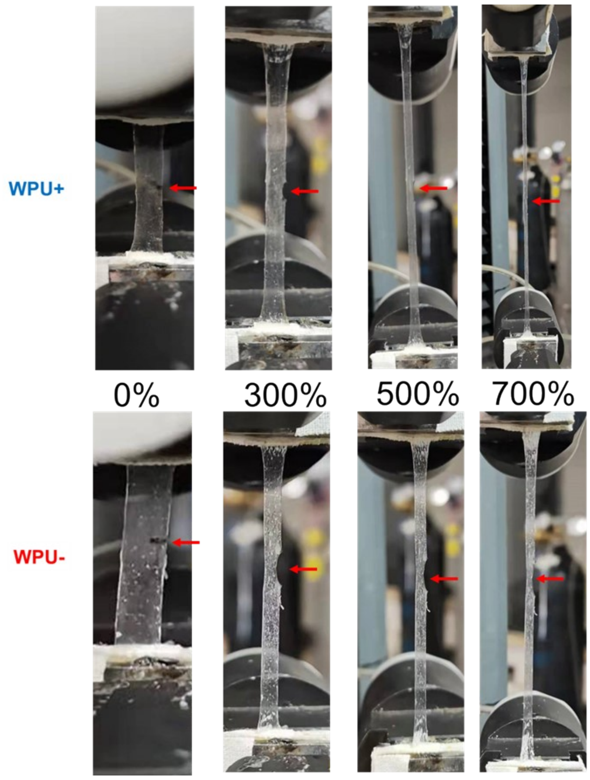

Figure S17. Images of the notched WPU+ and WPU- samples during stretching.

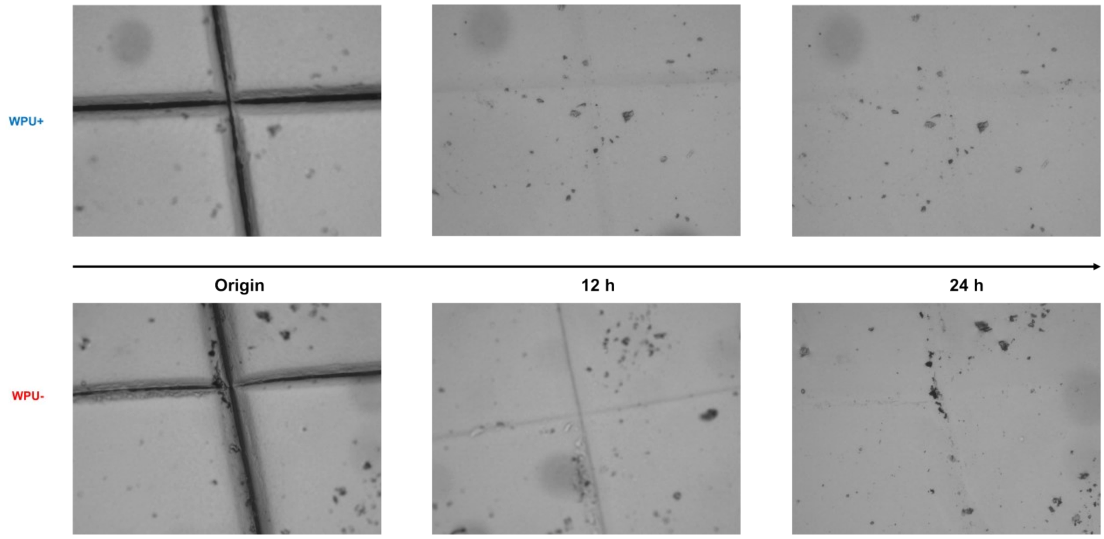

Figure S18. Optical microscope images of artificially scratched WPU+ and WPU- films in the healing process.

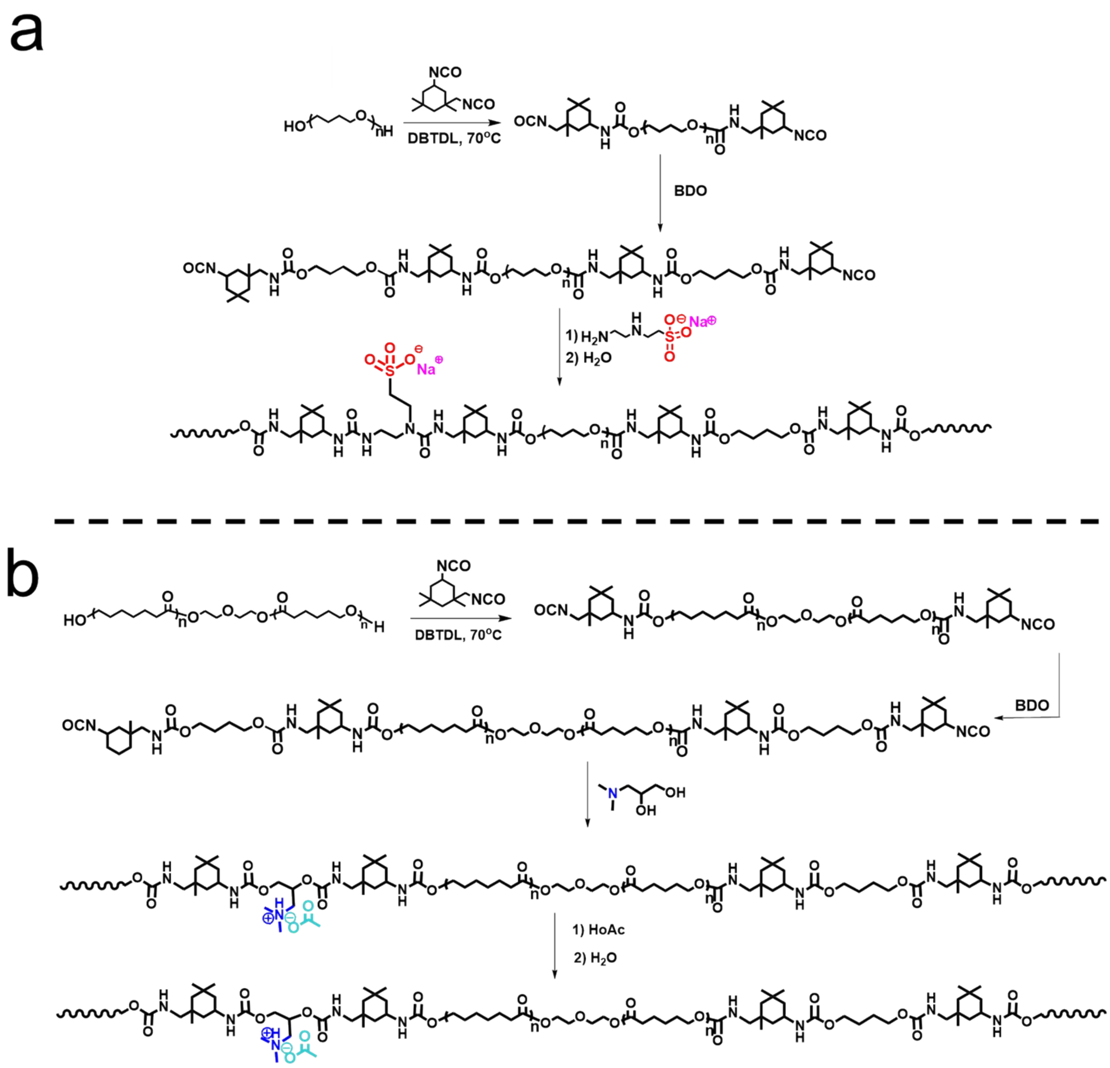

Figure S19. Synthesis and chemical structures of supramolecular (a) WPU_2- and (b) WPU_2+ elastomer.

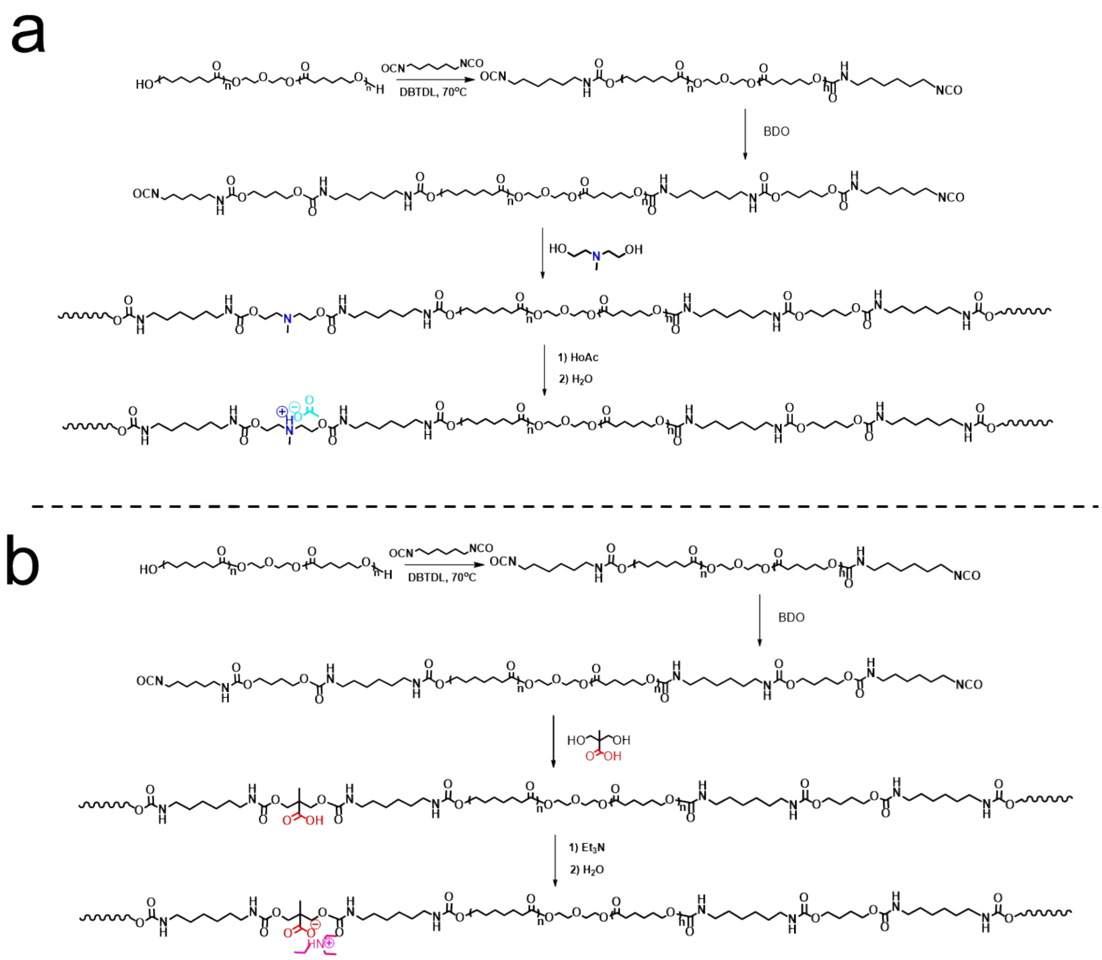

Figure S20. Synthesis and chemical structures of supramolecular (a) WPU_3+ and (b) WPU_3-elastomer.

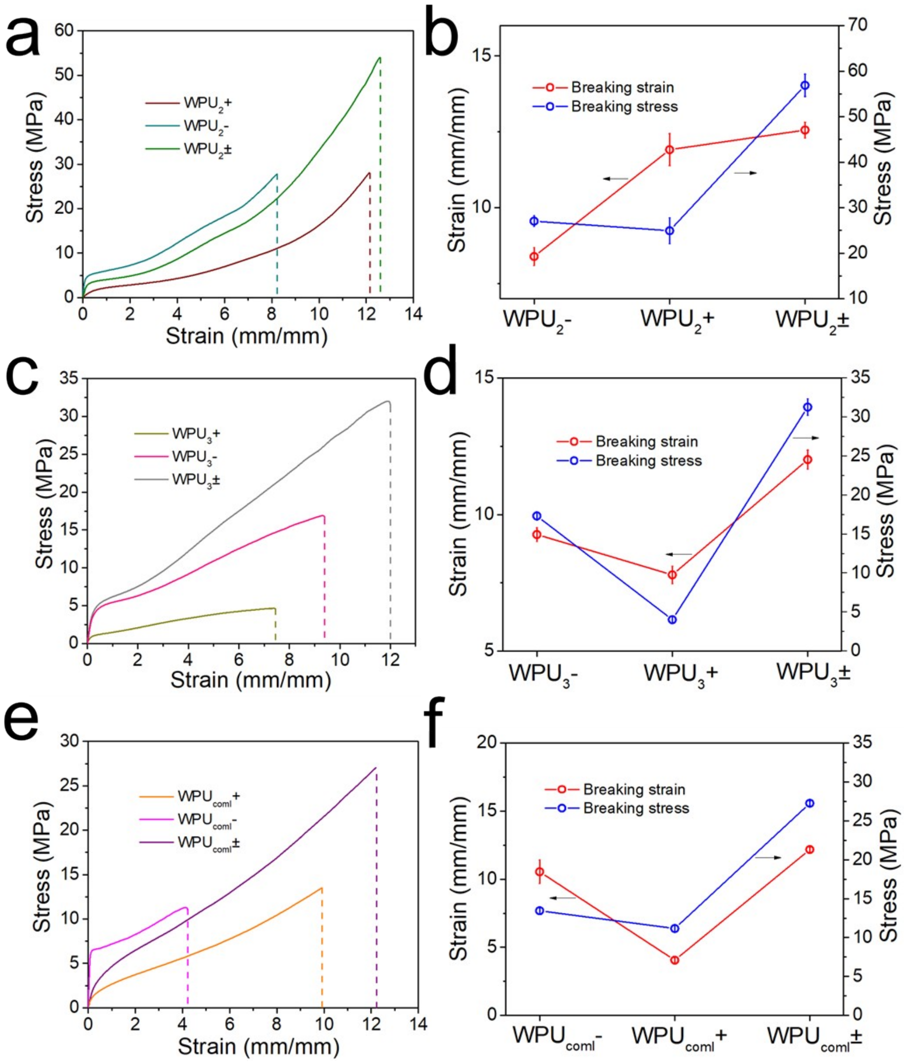

Figure S21. a) Stress–strain curves of WPU_2 elastomers. (n=3) b) Breaking strain and tensile strength of WPU_2 elastomers. c) Stress–strain curves of WPU_3 elastomers. (n=3) d) Breaking strain and tensile strength of WPU_3 elastomers. e) Stress–strain curves of WPU_{coml} elastomers. (n=3) f) Breaking strain and tensile strength of WPU_{coml} elastomers.

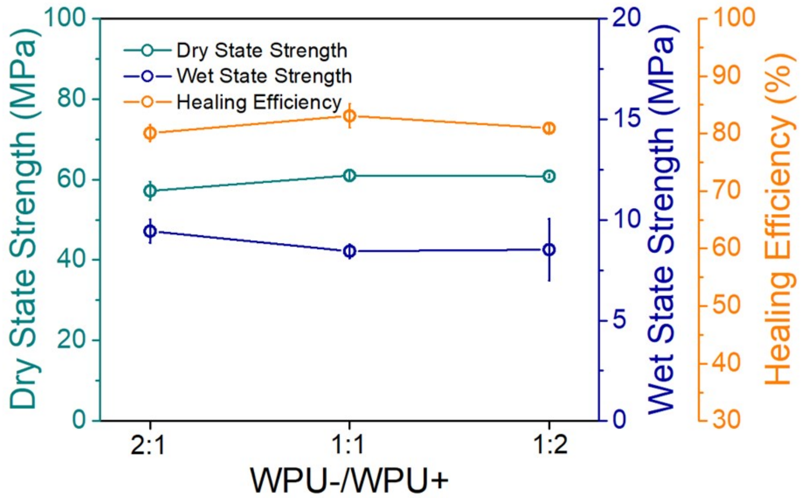

Figure S22. Dependences of the tensile strength, water resistance and healing efficiency of WPU± films on the ratio of WPU+ and WPU-.

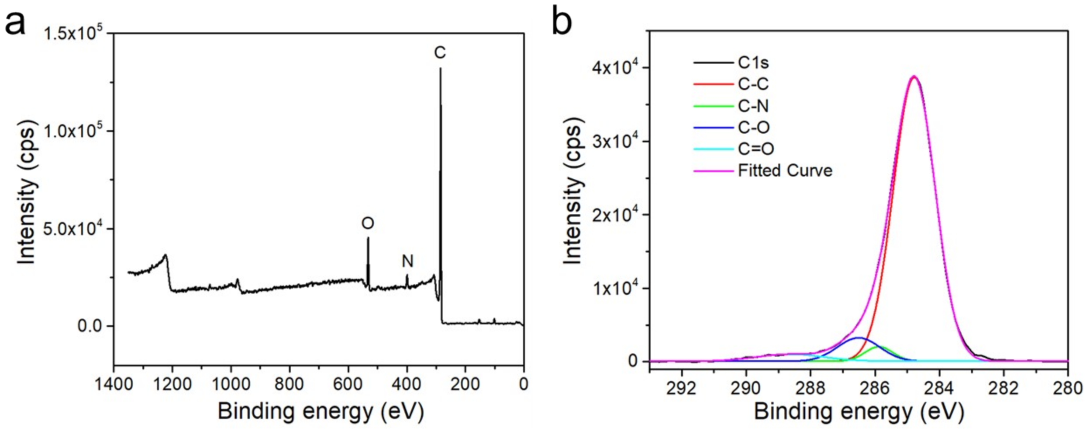

Figure S23. XPS spectra of the complexed WPU± : (a) survey scan spectra, (b) C1s spectra.

Table S1. Recipes used in the synthesis of the PU samples.

Sample	Polyol	Hydrophilic chain extender	BDO	Diisocyanate	Hard segment content
WPU+	4.00 g PCL	0.48g MDEA	0.09 g	2.40 g IPDI	42.6%
WPU-	4.00 g PCL	0.54g DMPA	0.09 g	2.40 g IPDI	43.1%
WPU_2+	4.00 g PCL	0.48g DMAPD	0.09 g	2.40 g IPDI	42.6%
WPU_2-	4.00 g PTMG	0.38 g AAS	0.09 g	1.87 g IPDI	36.9%
WPU_3+	4.00 g PCL	0.48g MDEA	0.09 g	1.61 g HDI	35.3%
WPU_3-	4.00 g PCL	0.54g DMPA	0.09 g	1.61 g HDI	35.9%

Table S2. The interaction energies among WPU+, WPU-, and water molecules.

Model	Interaction energy (kcal mol^{-1})
Water/Water	-4.5
Water/WPU+	-17.2
Water/WPU-	-12.5
WPU+/WPU+	-28.8
WPU-/WPU-	-33.7
WPU+/WPU-	-42.7

Supporting Movies

Movie S1. WPU± can be extruded directly as a hot melt adhesive, and the adhesive adheres firmly to the glass sheet even after withstanding violent water rinsing.

Movie S2. WPU± adhered aluminum sheet can lift 15 kg after immersing 30 days in water.

Movie S3. WPU+ adhered aluminum sheet cannot carry 15 kg after immersing 30 days in water.