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Supplementary Information

Biodegradable Polyurethane Non-tackifier Pressure-Sensitive Adhesive Derived from Cashew Nut Shells

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Experimental Section & Supplementary Text

Materials. Cardanol glycidyl ether (CGE) was provided by Chemifolio. Tetrahydrofuran (THF, 99.9%, anhydrous, Sigma-Aldrich), methanol (99.5%, Duksan), chloroform (99.8%, stabilized with ethanol, Duksan), triethylborane (TEB, 1.0 M in THF, Thermo Fisher), *tert*-butylimino-tris(dimethylamino)phosphorane (*t*-BuP$_1$, >97.0%, Sigma-Aldrich), glutaric anhydride (GA, 98%, Thermo Fisher), 1,4-benzenedimethanol (BDM, 99.0%, TCI), methylenediphenyl 4,4'-diisocyanate (MDI, >97%, TCI), 1,6-hexanediol (HDO, >97%, TCI), 1,4-diazabicyclo[2.2.2]octane (DBU, >99%, Sigma-Aldrich), Palladium on activated charcoal (Pd/C, Sigma-Aldrich), Celite® 545 (diatomaceous earth filtration aid, Sigma-Aldrich) were used as received. Poly(ethylene terephthalate) (PET) film, stainless steel panel, coater rods (70 μm) were purchased from ChemIntruments. Other chemicals were purchased from general vendors and used as received otherwise specified. All air- or moisture- sensitive chemicals were stored under an inert atmosphere in glove box.

Synthesis of P(GA-*alt*-CGE) (PGC). BDM (0.5 g, 3.64 mmol, 0.13 equiv.), GA (0.83 g, 7.29 mmol, 0.26 equiv.), THF (7 mL) were added to a flame-dried round-bottom flask under an inert atmosphere in a glove box and stirred until completely dissolved. Once dissolved, *t*-BuP$_1$ (1114 μL, 3.64 mmol, 0.13 equiv.) and TEB (1055 μL, 7.29 mmol, 0.26 equiv.) were added and stirred for 30 minutes. CGE (10 g, 28 mmol, 1 equiv.) was added, and the sealed flask was taken out of the glove box and placed in a 60 °C oil bath. Separately in the glove box, GA (2.36 g, 20.75 mmol, 0.74 equiv.) was dissolved in THF (3 mL), and the sealed vial was taken out of the glove box. The GA solution was added dropwise to the flask using a syringe pump over 30 min (100 μL min^{-1}). After 18 h, the polymer solution was precipitated into methanol to remove unreacted monomer and other impurities. The precipitated polymer was dried under vacuum at 40 °C for 48 h.

Synthesis of Polyurethanes (PUs). PUs were synthesized by a one-pot polymerization. In the argon-filled glove box, PGC (3.3 g, 1 mmol, 1 equiv.), DBU (29.87 μL, 0.2 mmol, 0.2 equiv.) and THF (7 mL) were charged into a dry round-bottom flask. The flask was sealed, taken out of the glove box, and placed in a 60 °C oil bath. A solution of MDI in THF (3.5 mL), separately prepared in the glove box, was transferred to a syringe, and added dropwise into the vigorously stirred PGC solution over 1 h (58 μL min^{-1}). After 2 h, a solution of HDO in THF (3.5 mL), similarly prepared and loaded into a syringe, was added dropwise under the same conditions.

The reaction mixture was stirred for additional 16 h at 60 °C and 300 rpm. The product was precipitated into methanol and dried under vacuum at 40 °C for 48 h. The resulting PUs were denoted PU-#, where # corresponds to the molar ratio of MDI to PGC. For example, PU-2 refers to a formulation with a PGC:MDI molar ratio of 1:2.

Hydrogenation of PGC (H-PGC) and PU-2 (H-PU-2). Unsaturated PGC or PU-2 (2 g), Pd/C (600 mg), and THF (30 ml) were charged into a round-bottom flask and sealed with a rubber septum. The system was purged with argon gas for 10 min to remove residual oxygen and purged with hydrogen using hydrogen-filled balloons. The reaction mixture was stirred at room temperature for 48 h. The crude mixture was filtered through Celite® 545 (diatomaceous earth filtration aid) and neutral alumina to remove the Pd/C catalyst. The filtrate was concentrated under reduced pressure to remove THF, and the residue was precipitated into methanol. The precipitated polymer was collected and dried under vacuum at 40 °C for 48 h.

Adhesive testing. Polyurethane polymers were dissolved in chloroform (0.25 g mL^{-1}), and the solution was cast onto a PET film using a bar coater (target wet thickness, 70 μm), followed by drying at 70 °C for 20 min. The cast film was stored in a low-pressure desiccator prior to adhesive testing. In the case of using a tackifier, the tackifier was dissolved together with the polyurethane in chloroform, and the subsequent procedure remained the same.

Peel test. Peel adhesion tests were performed using a 180° Peel Adhesive Testing Machine (PA-1000-180, ChemInstruments, Inc.), following ASTM D3330 (Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape). Adhesive samples were cut into 1 inch strips and adhered to stainless steel test panels using a 4.5 lb ASTM-quality hand roller. Each sample was tested at least three times at a peel rate of 305 mm min^{-1}. The peel force was recorded as the maximum measured force and averaged across the samples.

Probe tack test. Probe tack tests were performed using a PT-1000 Polyken Probe Tack Tester (ChemInstruments, Inc.), following ASTM D2979 (Standard Test Method for Pressure-Sensitive Tack of Adhesives Using an Inverted Probe Machine). Adhesive samples were cut into 0.8 cm × 0.8 cm squares and contacted with a probe of 5 mm diameter. Each sample was tested at least three times at a probe rate of 610 mm min^{-1}. The probe tack force was recorded as the maximum measured force and averaged across the samples.

Degradation experiment. PUs were dissolved in THF (8 mg mL^{-1}). A 0.1 M NaOH aqueous solution was added to the solution, yielding 4 mg mL^{-1}.The solution was stirred at room temperature, and the aliquot was taken at the predetermined time intervals. The solvent was evaporated overnight in the vacuum oven, and the remaining polymers (or degradation products) were analyzed by ^{1}H NMR spectroscopy and SEC.

Characterizations.

Nuclear magnetic resonance (NMR). NMR spectroscopy data were obtained at Inha University a 400 MHz Bruker Avance III. All NMR data were analyzed by using the TopSpin (Bruker).

Size exclusion Chromatography (SEC). SEC was performed in THF (40 °C, 1.0 mL min^{-1}) using GPC equipped with KF-806L column (Shodex) and a refractive index (RI) detector. The molar mass and dispersity ($Đ$) were determined and calibrated using polystyrene standards.

Fourier transform infrared (FT-IR) spectroscopy. FT-IR spectra of samples were measured using an IR Affinity-1S spectrometer (Shimadzu, Japan) in ATR mode. Measurements were conducted over the range of 500 – 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

Differential scanning calorimetry (DSC). DSC were performed using a PerkinElmer DSC6000. 2–3mg of sample was loaded into hermetically sealed aluminum pans for measurement. The thermal history of all the samples was removed by the first heating (10 °C min^{-1}) to 200 °C followed by the quenching to –70 °C (10 °C min^{-1}). All the DSC thermograms shown in this paper are the second heating thermograms (20 °C min^{-1}).

Thermogravimetric analysis (TGA). TGA was performed using a TGA Q50 thermogravimetric analyzer under a nitrogen gas flow. The measurements were carried out at a heating rate of 10 °C min^{-1}.

Rheological properties. A Discovery Hybrid Rheometer (NFEC-2024-09-299197, TA Instruments, USA) was used to evaluate the viscoelastic response of polymers. Prior to all measurements, the linear viscoelastic region was determined for each sample by conducting dynamic strain sweep experiments. PU-2, PU-2.5 and PU-3 were analyzed using an 8 mm parallel-plate fixture, while a 25 mm parallel-plate fixture was used for PU-1 and PU-1.5 due to their low modulus. Temperature sweeps were conducted from 80 °C to –30 °C at a cooling rate of 10 °C min^{-1} under conditions of 1 rad s^{-1} frequency and 1% strain. Frequency sweeps were performed from 100 rad s^{-1} to 0.01 rad s^{-1} at 25 °C with 1% strain. For time–temperature superposition (TTS) analysis, frequency sweeps were conducted at a constant strain 10% across a temperature range of –30 °C to 80 °C, in 10 °C intervals.

Gas chromatography-Flame Ionization Detector (GC-FID). GC-FID was performed using an Agilent 7890 with a split flame ionization detector and split injector. All solvents were separated on an RTX 65 TG column. The injector temperature was 300 °C with a split ratio of 50:1. The detector temperature was 330 °C. The oven program was 240 °C (held for 5 min) followed by heating at 2 °C min–1 to 280 °C.

Calculation of Bio Carbon content (%). Bio carbon content (%) was measured using Method B (AMS) of the standard ASTM D6866-24. percent Modern Carbon (pMC) is a value measured using an acceleration mass spectrometer, and the sample was graphitized using IONPLUS's AGE3 (graphitizer) for pretreatment of the sample. The atmospheric correction factor was applied at 99.4 pMC, which is the value corresponding to 2025 in ASTM D6866-24. Biocarbon content is calculated based on TC (Total Carbon).

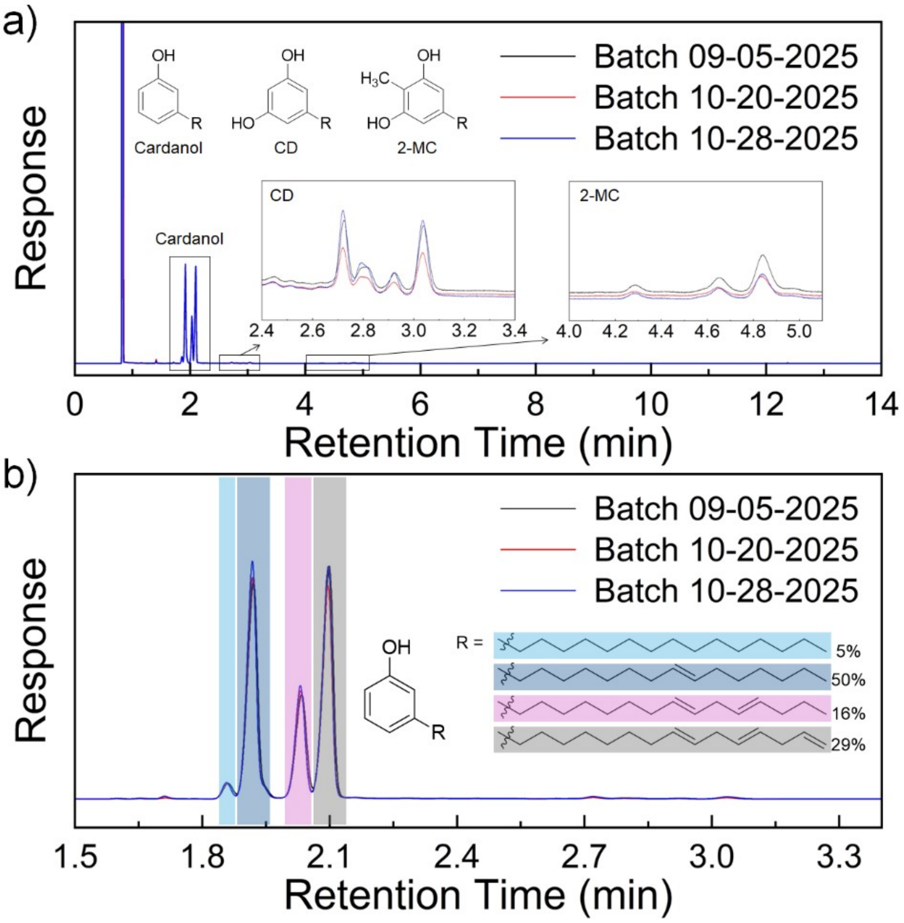

Figure S1. (a) Full GC data of multiple commercial cardanol batches. (b) Magnified GC region corresponding to cardanol fraction in (a).

Since the variation of unsaturated alkyl chains – mono/di/tri-unsaturation distribution – may influence polymer properties, cardanols from three independent batches from the industrial supplier were analyzed by gas chromatography (GC). All batches exhibited highly consistent unsaturation profiles, dominated by mono-, di-, and tri-unsaturated C15 chains, with <5% saturated chains. Minor components such as 2-methylcardol (2-MC) and cardol (CD) were detected only at trace levels that are unlikely to affect polymerization or final properties. Given that the epoxidation step does not modify the alkyl-chain unsaturation distribution, the CGE used in this study is expected to succeed the same batch-to-batch consistency observed for the parent cardanol. This conclusion is further supported by the reproducible NMR structures, molecular weights, and adhesion/rheology measurements obtained from CGE batches used throughout the study.

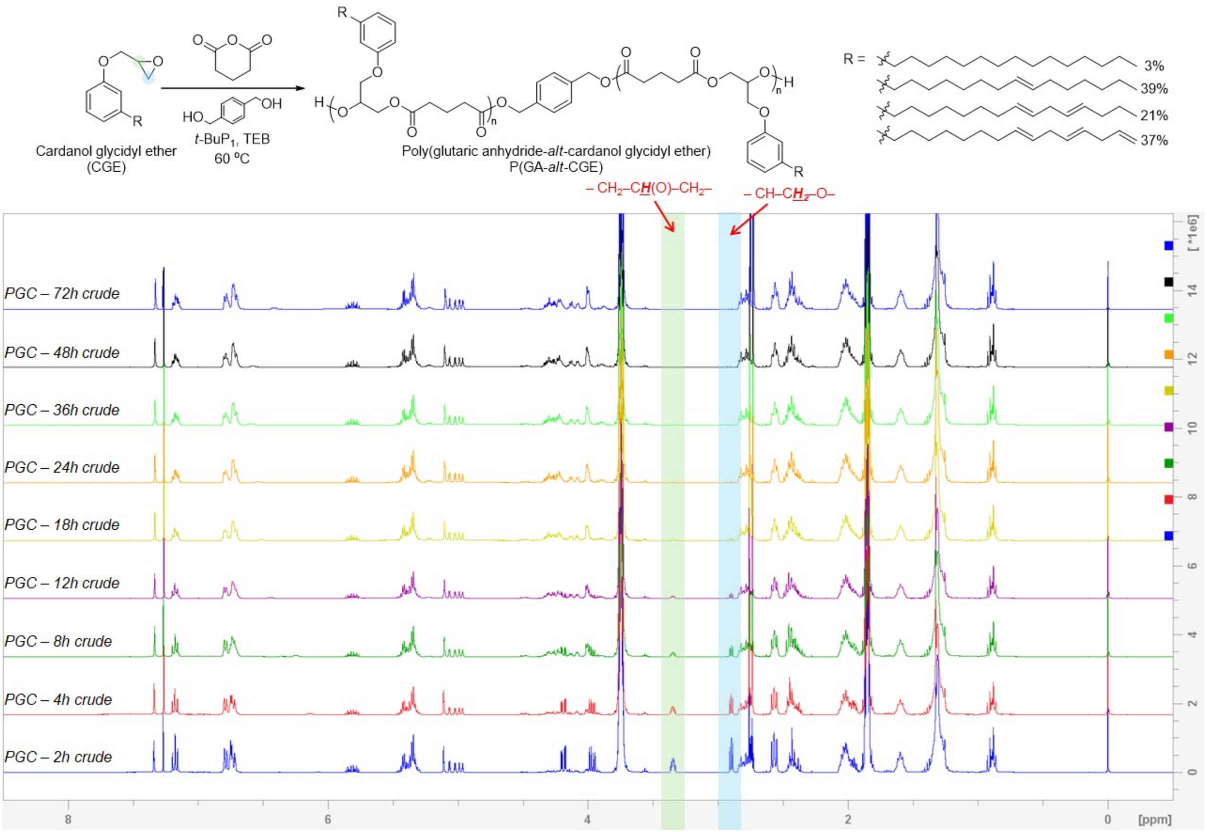

Figure S2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) for the polymerization at 60 °C, $[CGE]_0 = 2.8$ M, $[GA]_0 = 2.8$ M, $[BDM]_0 = 0.364$ M. The epoxide proton signals (2.9–3.4 ppm) decrease as the polymerization proceeds.

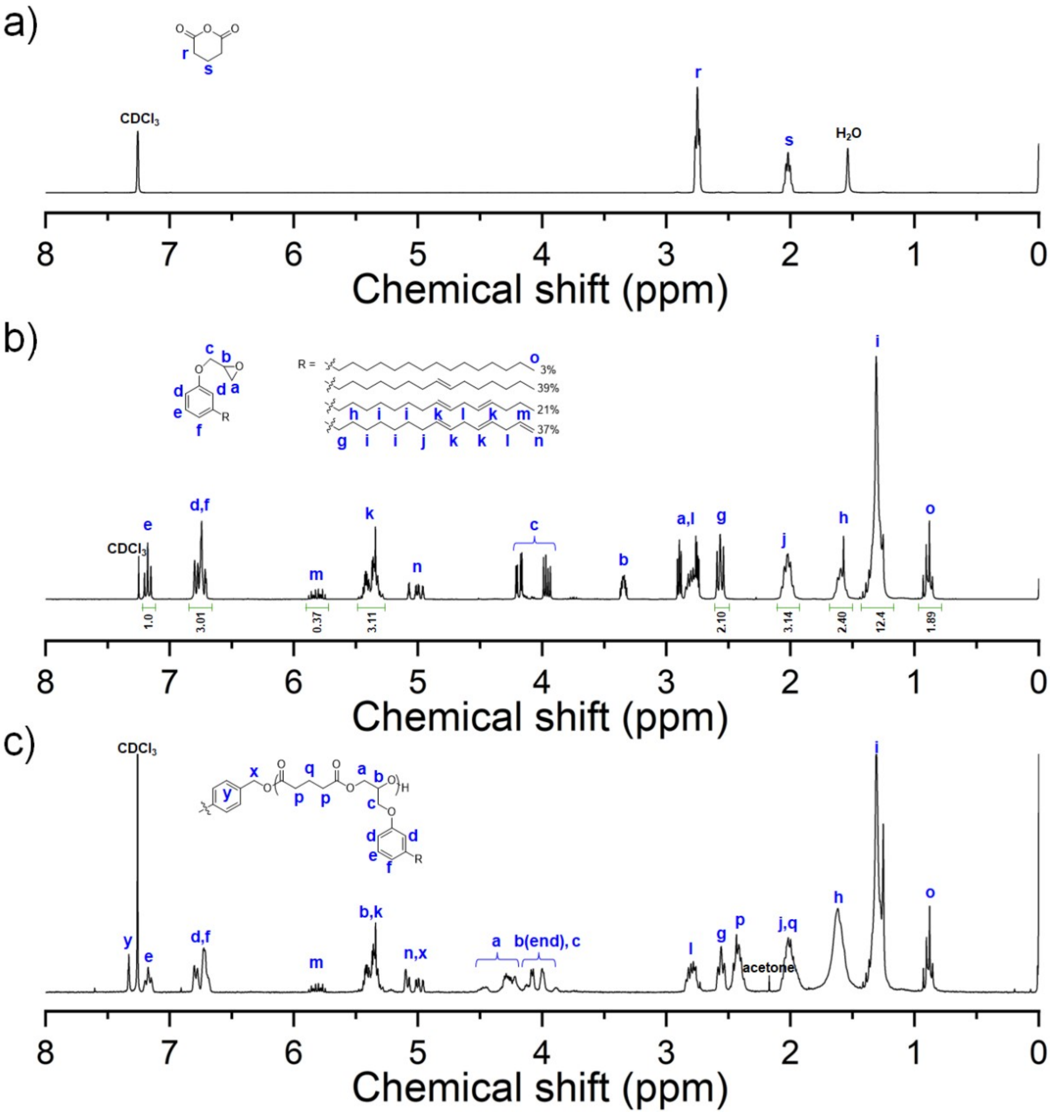

Figure S3. Full ^{1}H NMR spectra (400 MHz, $CDCl_3$) of GA, CGE and PGC.

Fig S3b: To accurately determine the alkyl chain distribution, we used peak e as the internal reference standard. By normalizing all the peaks relative to peak e =1, we calculated the relative fractions of saturated (x), mono-unsaturated (y), di-unsaturated (z), and tri-unsaturated (w) alkyl chains, where $x + y + z + w = 1$. The experimentally obtained integration values and corresponding equations are as follows:

- Peak m = $w = 0.37$
- Peak k = $2y + 4z + 4w = 3.11$
- Peak j = $2(2y + 2z + w) = 3.14$
- Peak o = $3(x + y + z) = 1.89$

By solving this system of equations, we obtained the following relative fractions of the alkyl side chains: saturated (x=3%), mono-unsaturated (y=39%), di-unsaturated (z=21%), and tri-unsaturated (w=37%).

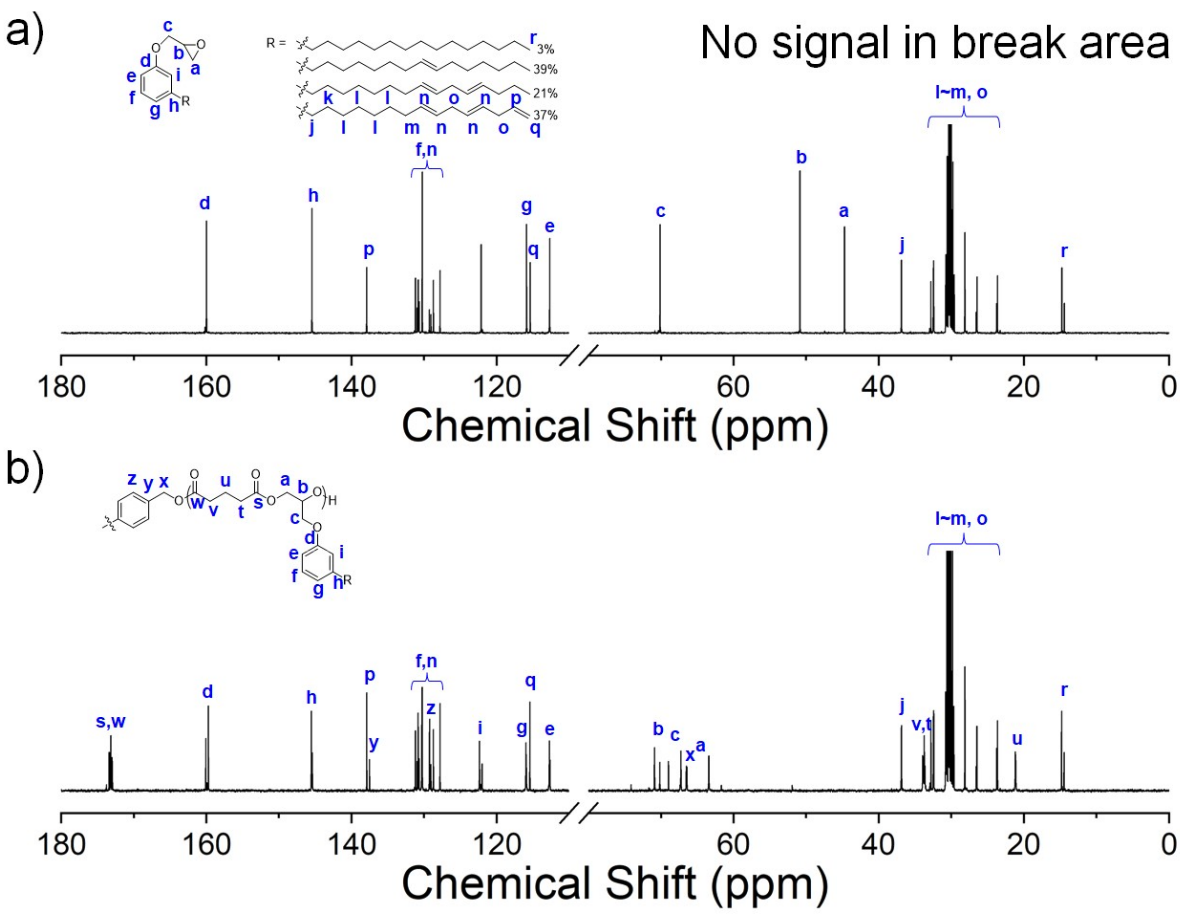

Figure S4. Full ^{13}C NMR spectra (400 MHz, acetone-d_6) of CGE and PGC.

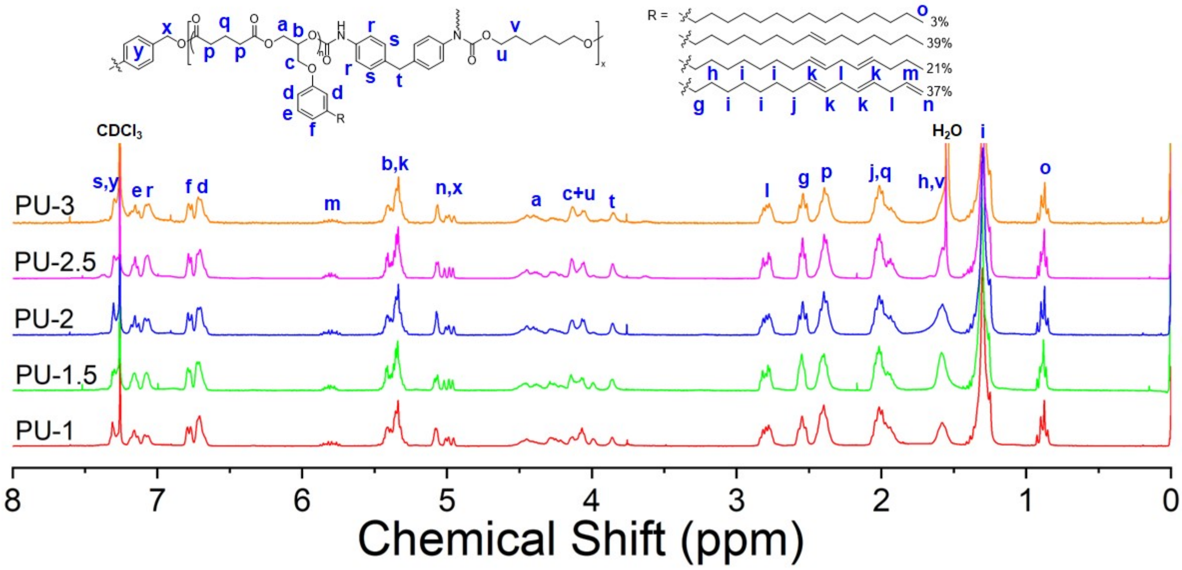

Figure S5. Full ^{1}H NMR spectra (400 MHz, CDCl$_3$) of PUs.

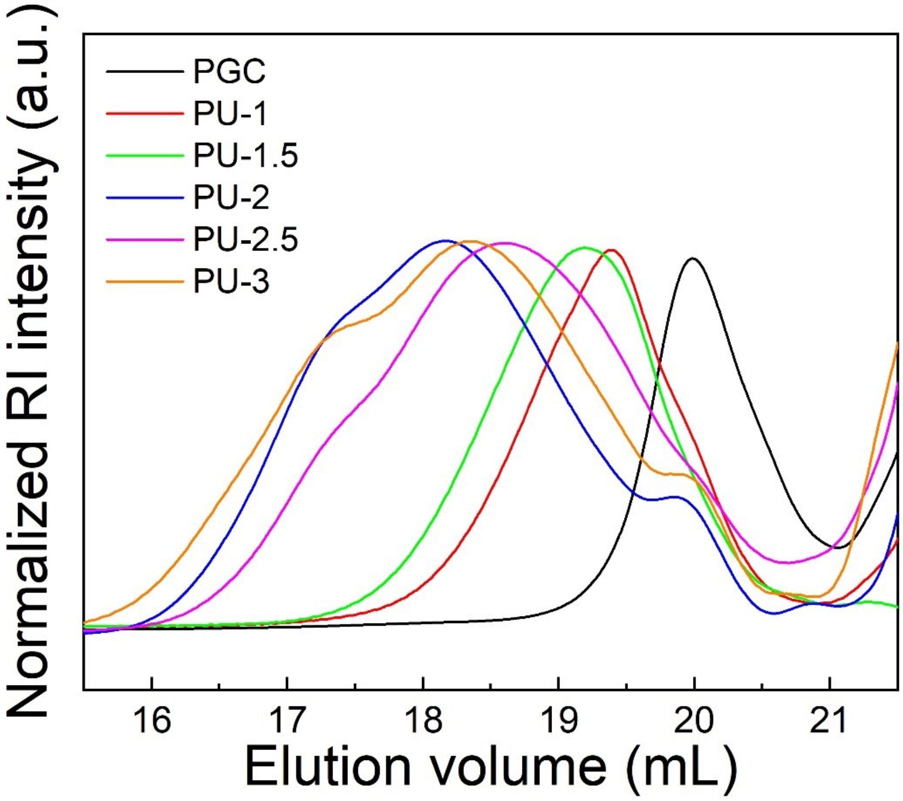

Figure S6. SEC chromatograms of the PGC and PUs (THF, 40 °C).

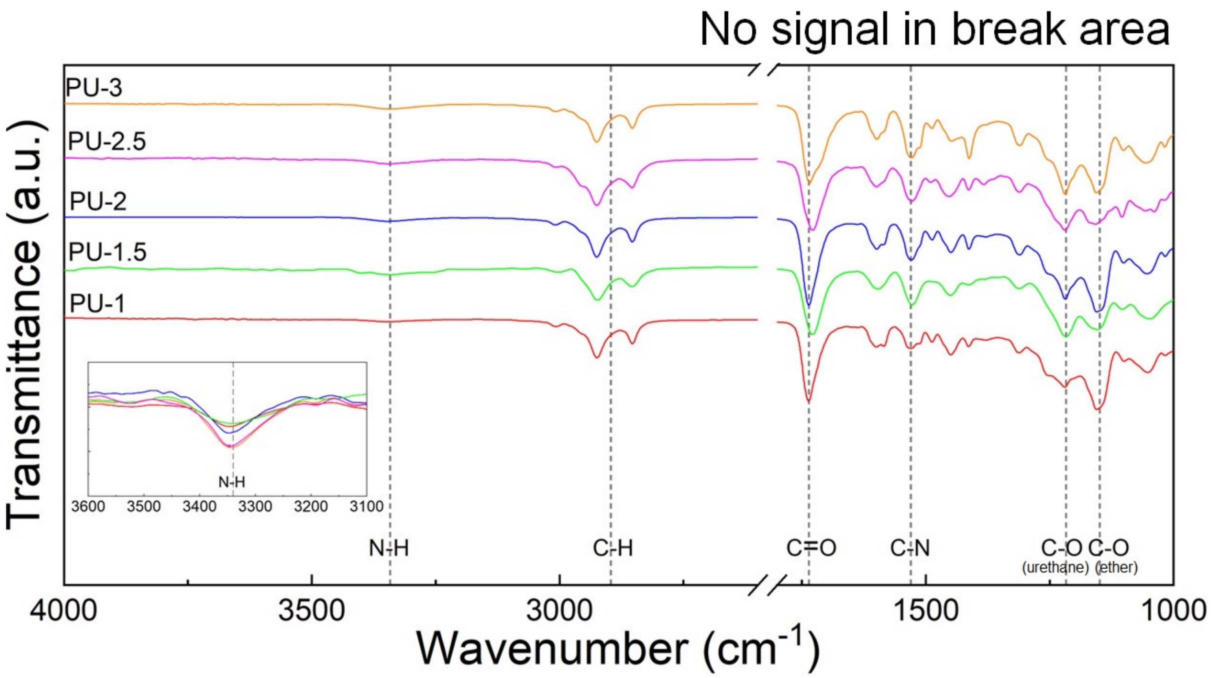

Figure S7. Full FT-IR spectra of PUs.

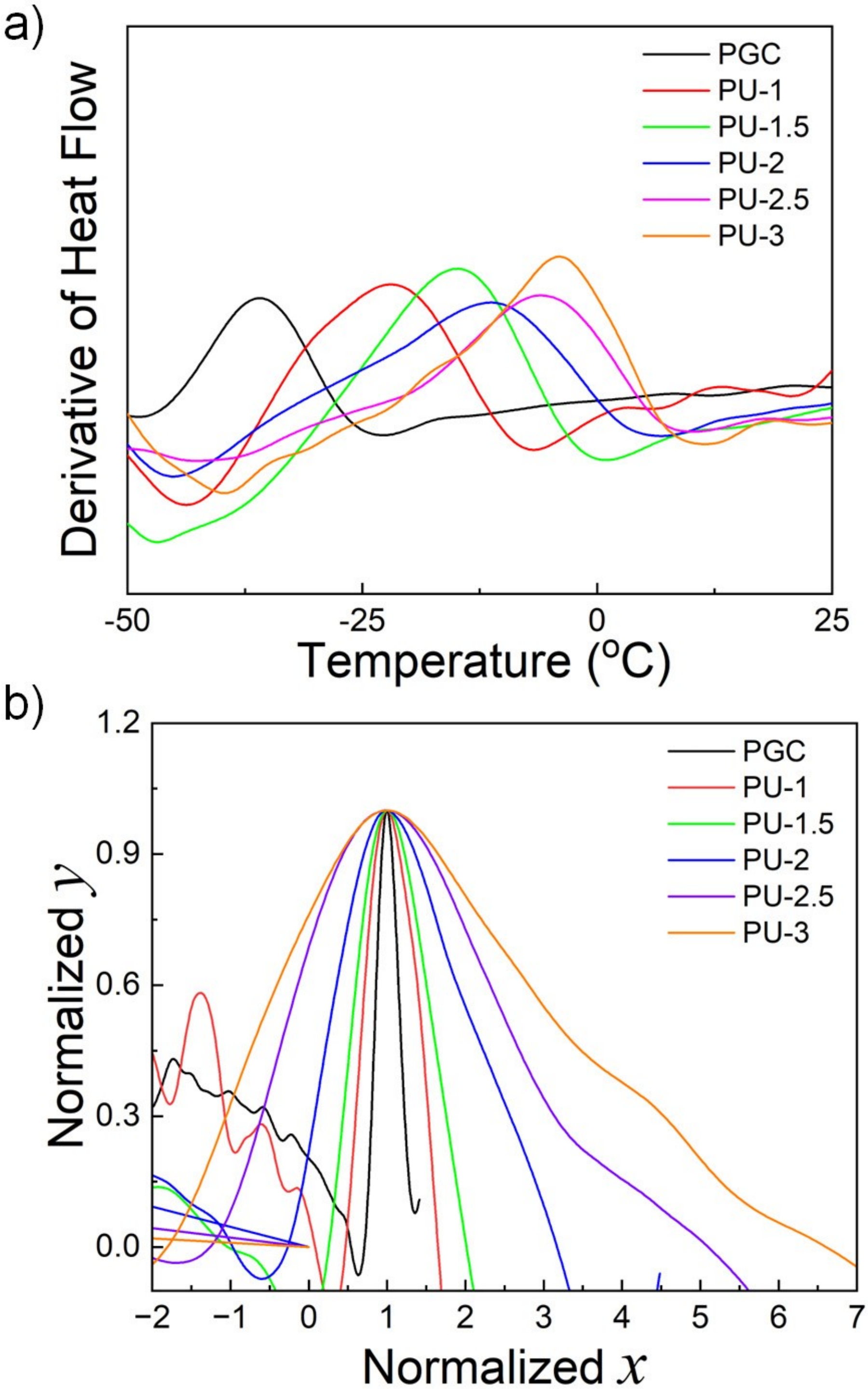

Figure S8. (a) 1st derivative DSC curves (2nd heating, 10 °C min $^{-1}$) of the PGC and PUs. (b) Normalized curves for direct comparison of T_g broadness.

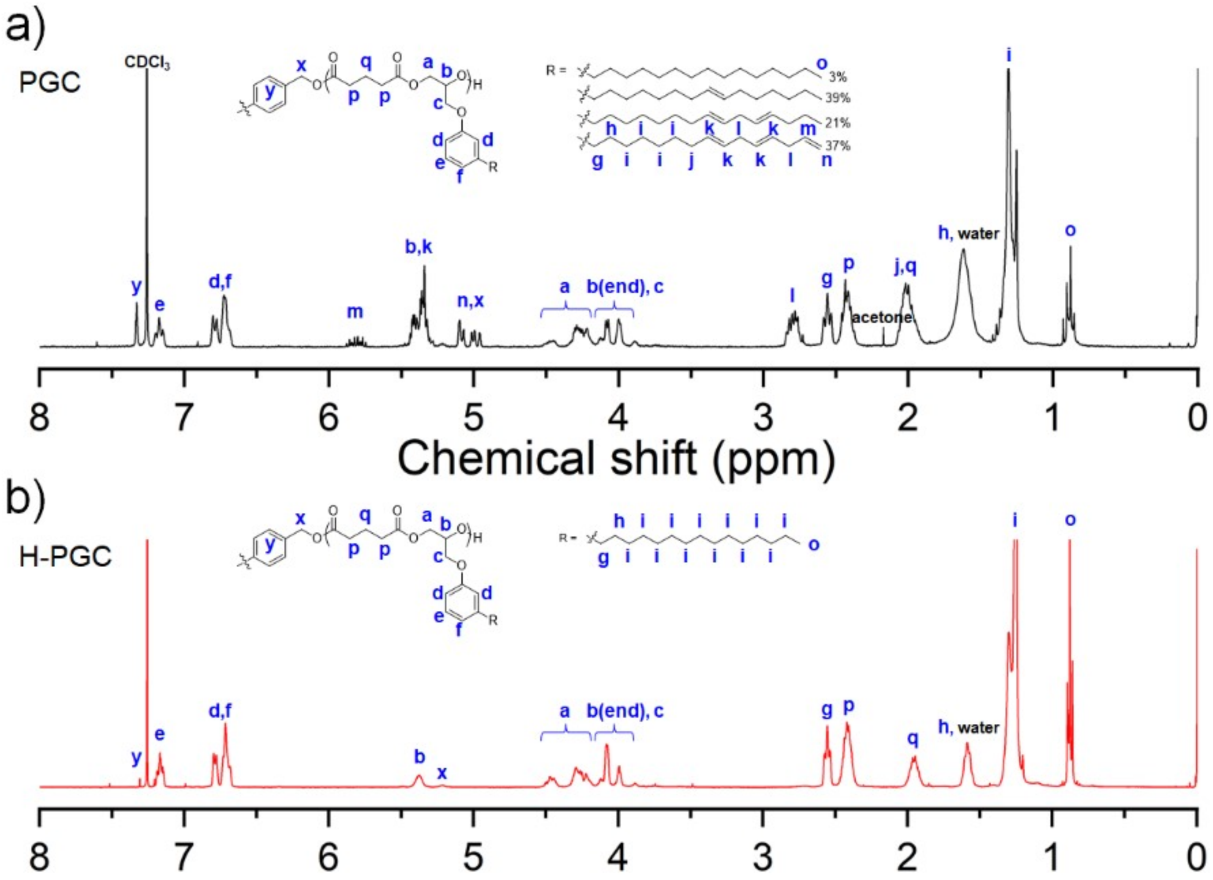

Figure S9. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the PGC and H-PGC.

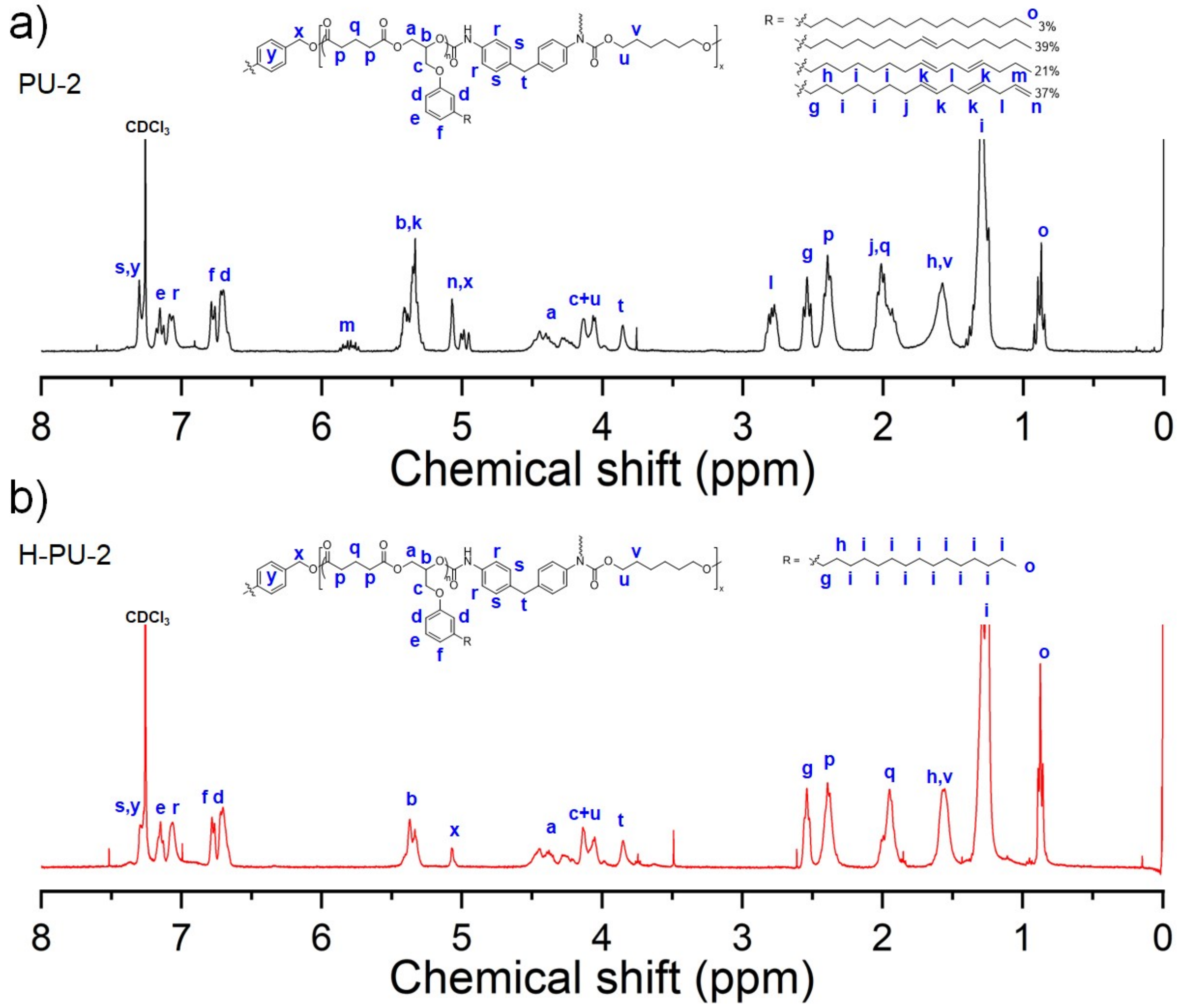

Figure S10. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the PU-2 and H-PU-2.

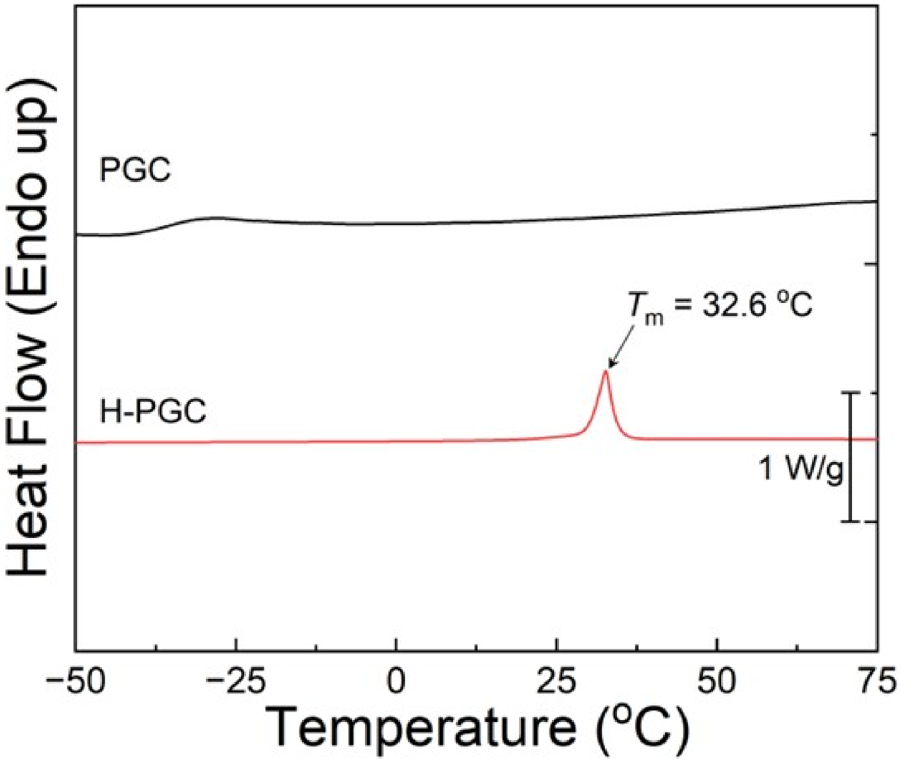

Figure S11. DSC data (2nd heating, 10 °C min^{-1}) of the PGC and H-PGC

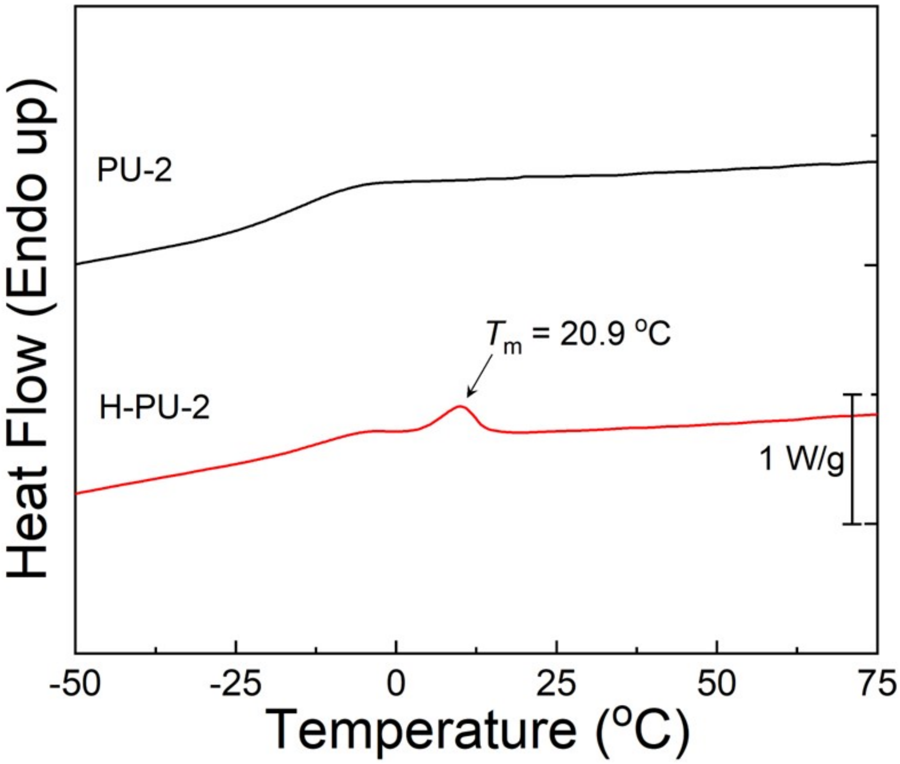

Figure S12. DSC data (2nd heating, 5 °C min^{-1}) of the PU-2 and H-PU-2.

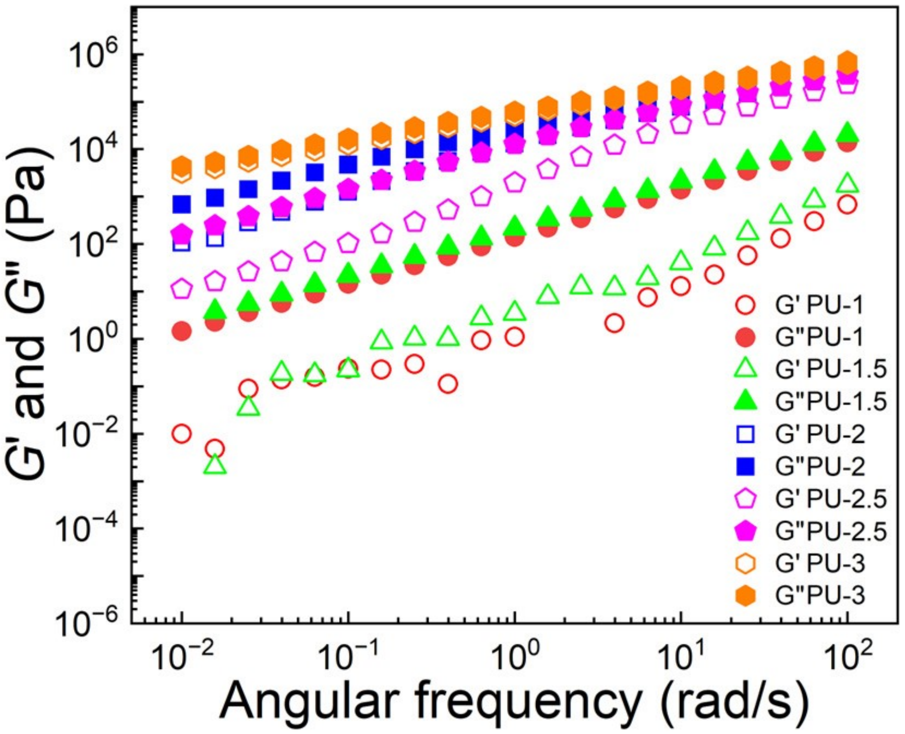

Figure S13. Storage and loss moduli (100 rad s^{-1} to 0.01 rad s^{-1}, 25 °C) of the PUs.

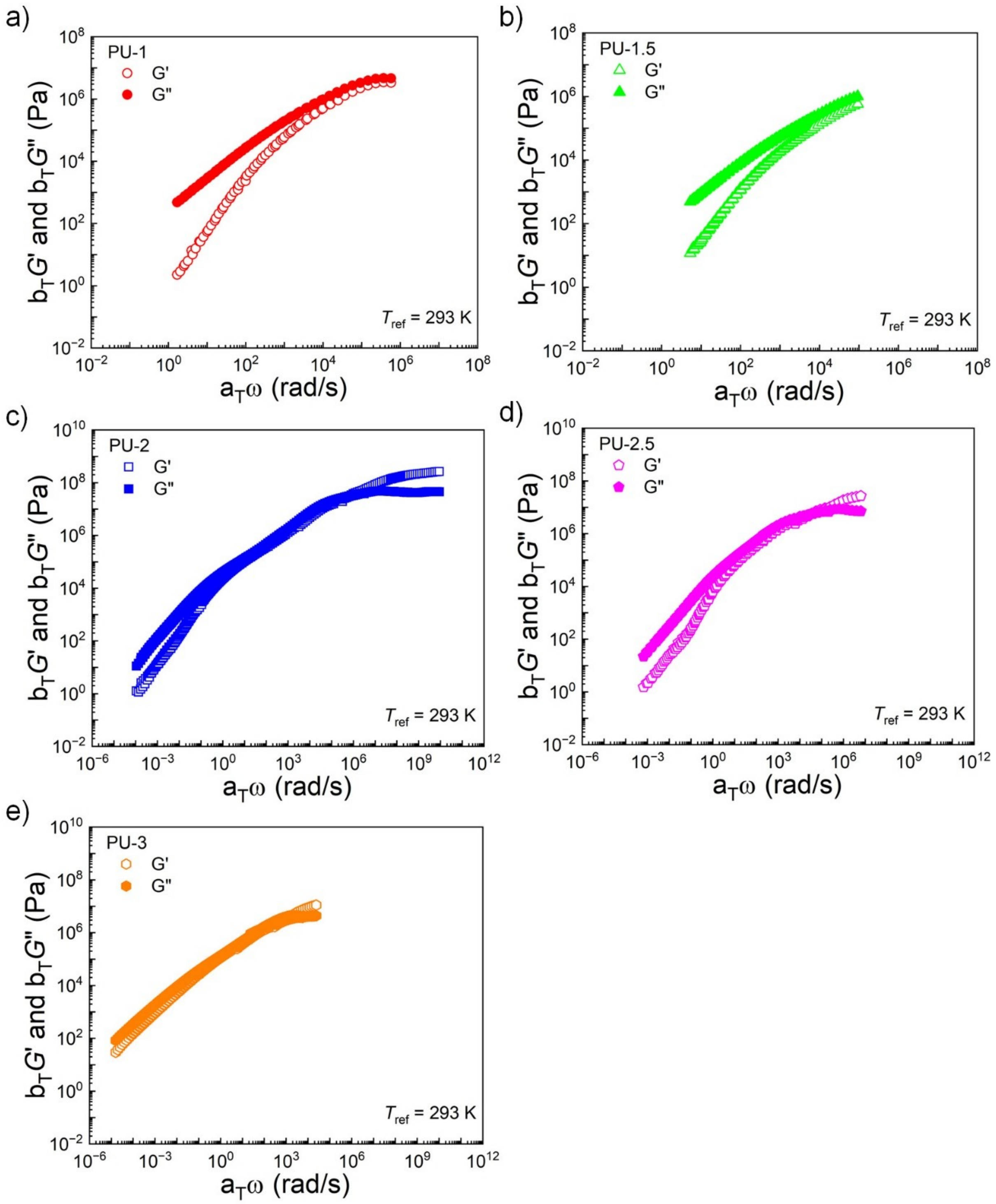

Figure S14. Time–temperature superposition (TTS) master curves of storage modulus (G'), loss modulus (G'') for the PUs ($T_{\mathrm{ref}} = 293$ K).

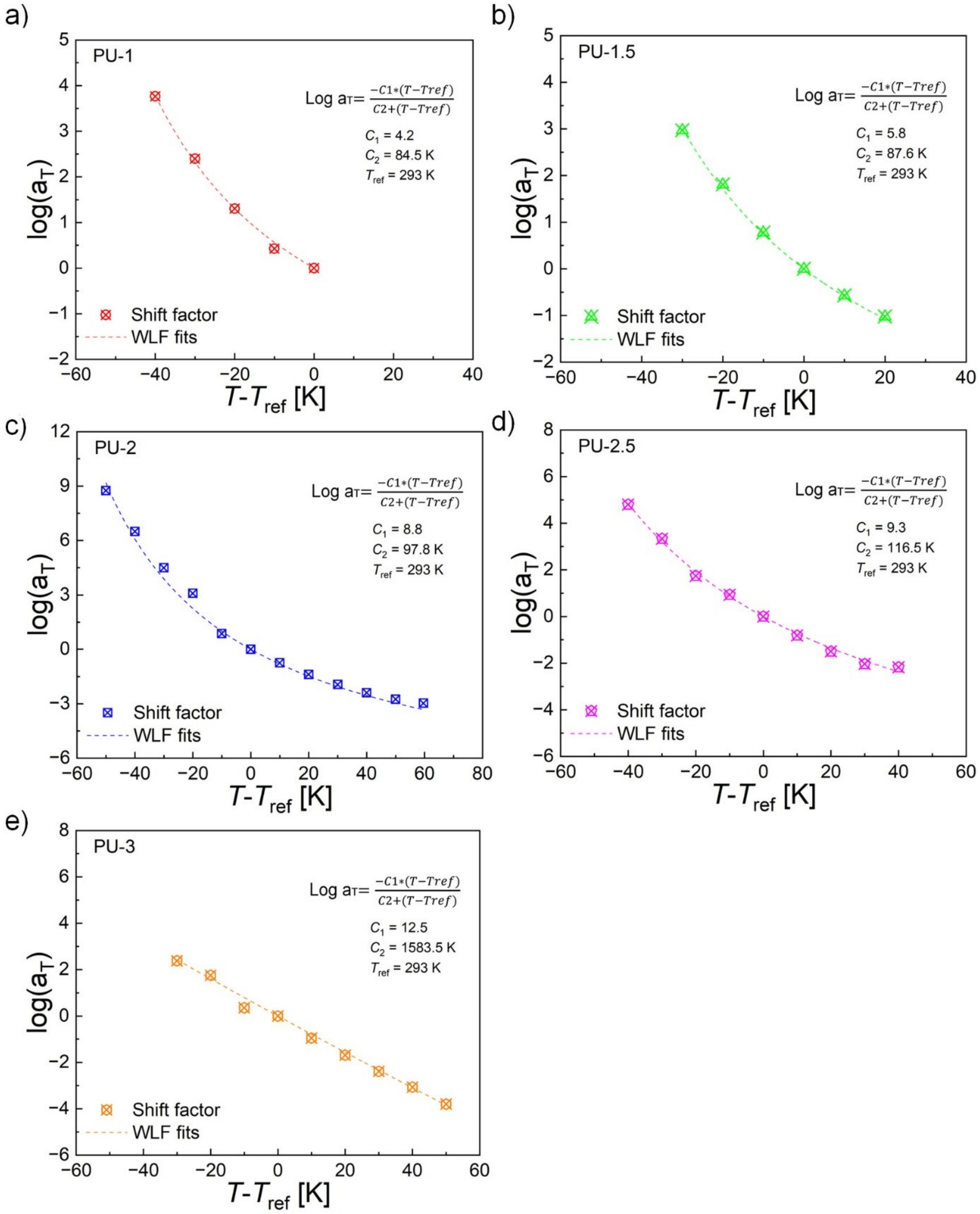

Figure S15. Temperature dependence of shift factors a_T from time–temperature superposition analysis with WLF model fits for PUs (T_{ref} = 293 K).

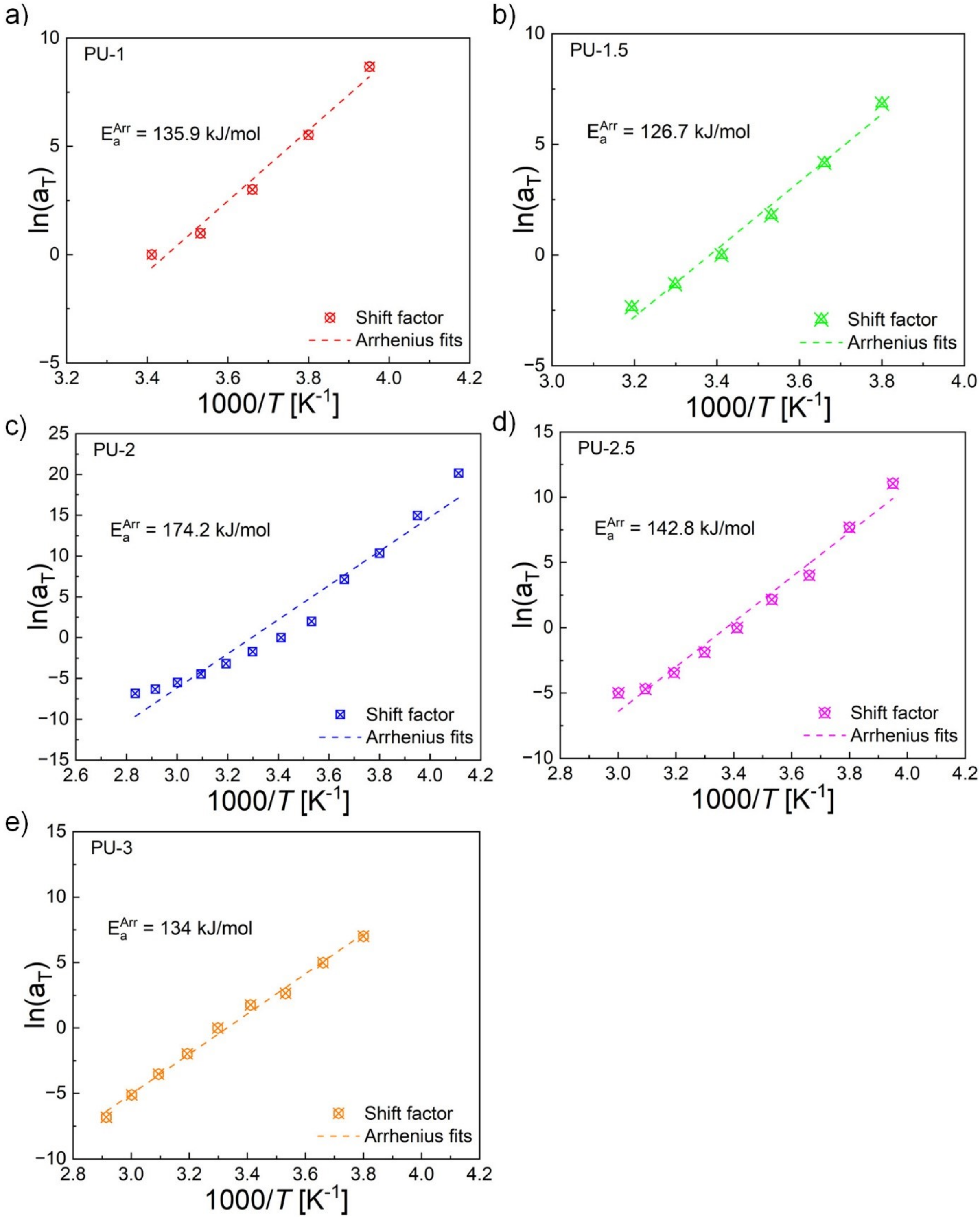

Figure S16. Temperature dependence of shift factors a_T from time–temperature superposition analysis with Arrhenius model fits for PUs (T_{ref} = 293 K).

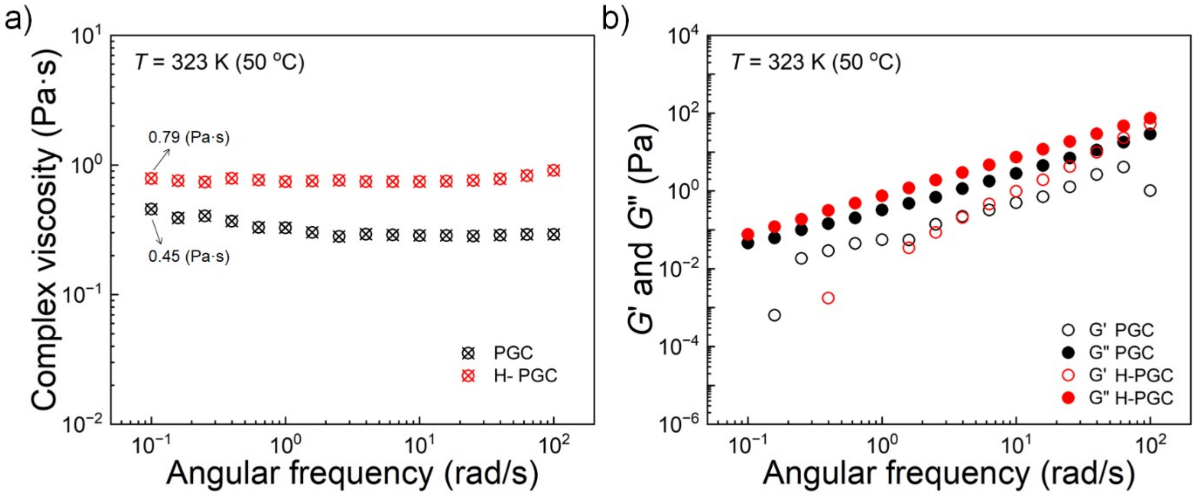

Figure S17. (a) Complex viscosity (100 rad s^{-1} to 0.1 rad s^{-1}) and (b) storage and loss moduli (100 rad s^{-1} to 0.1 rad s^{-1}) of the PGC and H-PGC at 50 °C.

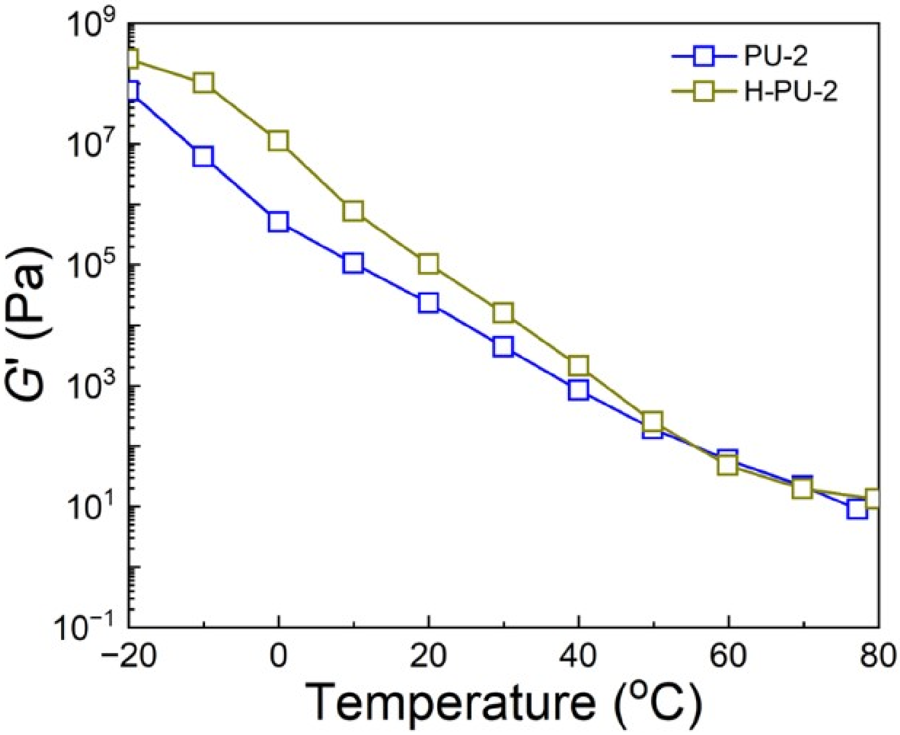

Figure S18. Storage moduli (G', cooling, 10 °C min^{-1}, 1 rad s^{-1}) of the PU-2 and H-PU-2.

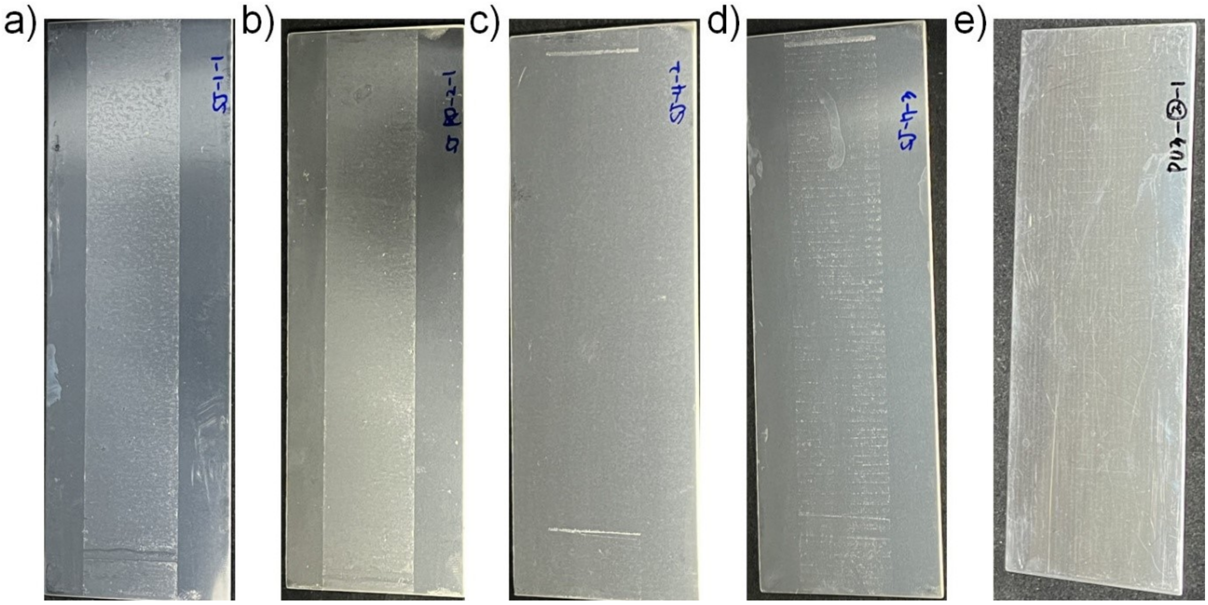

Figure S19. Photographic images showing removal behavior and failure modes of PU PSAs after 180° peel test from stainless steel substrate.; (a) PU-1, (b) PU-1.5, (c) PU-2, (d) PU-2.5, and (e) PU-3. Images show that (a, b) exhibited cohesive failure with adhesive residues remaining on the substrate, while (c-e) showed adhesive failure characterized by clean removal without residue.

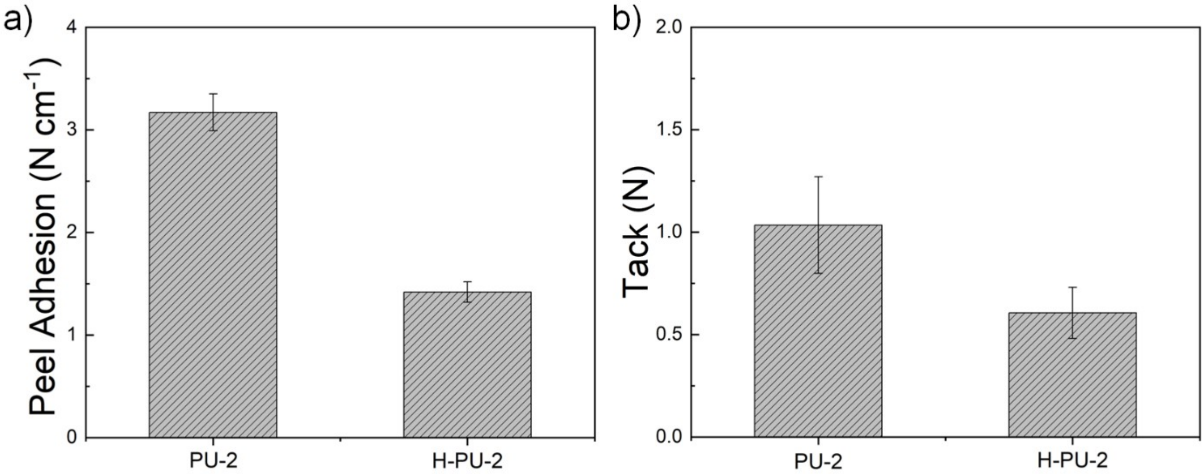

Figure S20. Adhesion properties of PU-2 and H-PU-2: (a) peel adhesion test, (b) probe tack test.

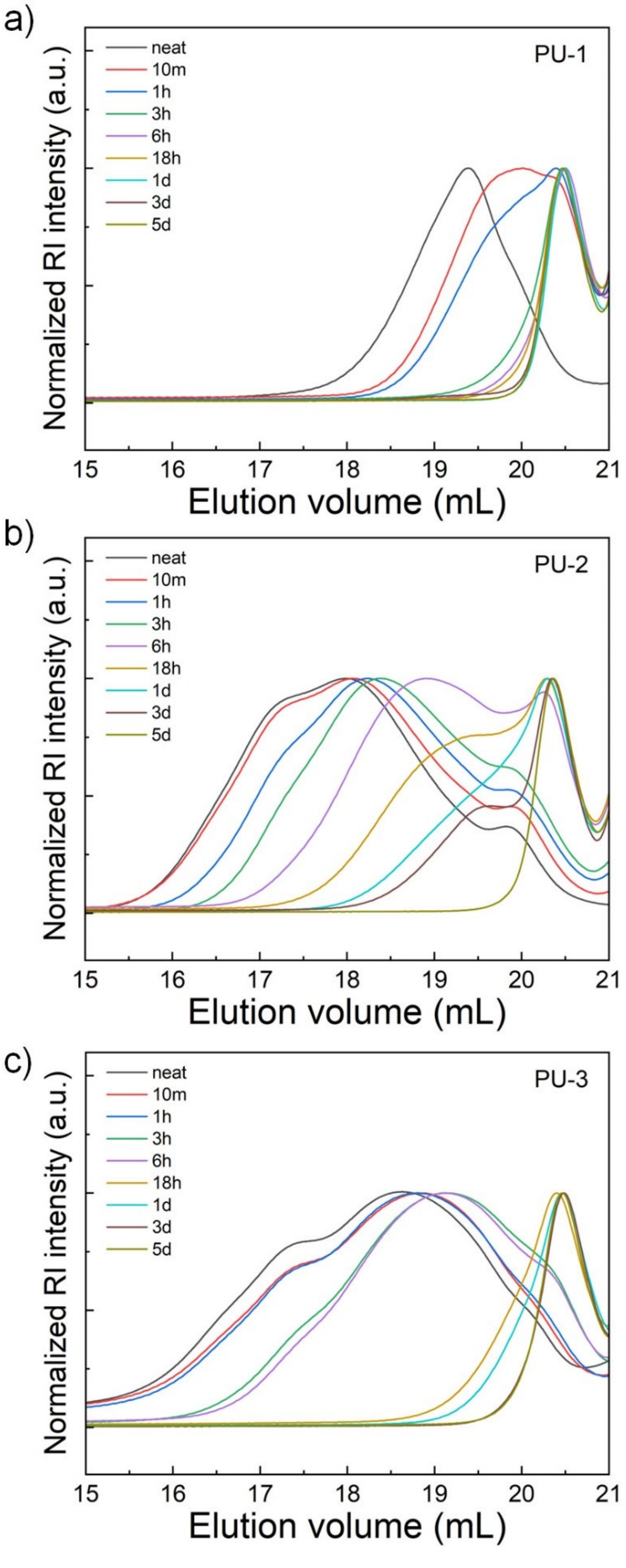

Figure S21. SEC trace of PU-1, PU-2 and PU-3 under the hydrolytic degradation conditions at room temperature in 0.1 M NaOH(*aq.*)/THF mixture solution (1/1 vol.).

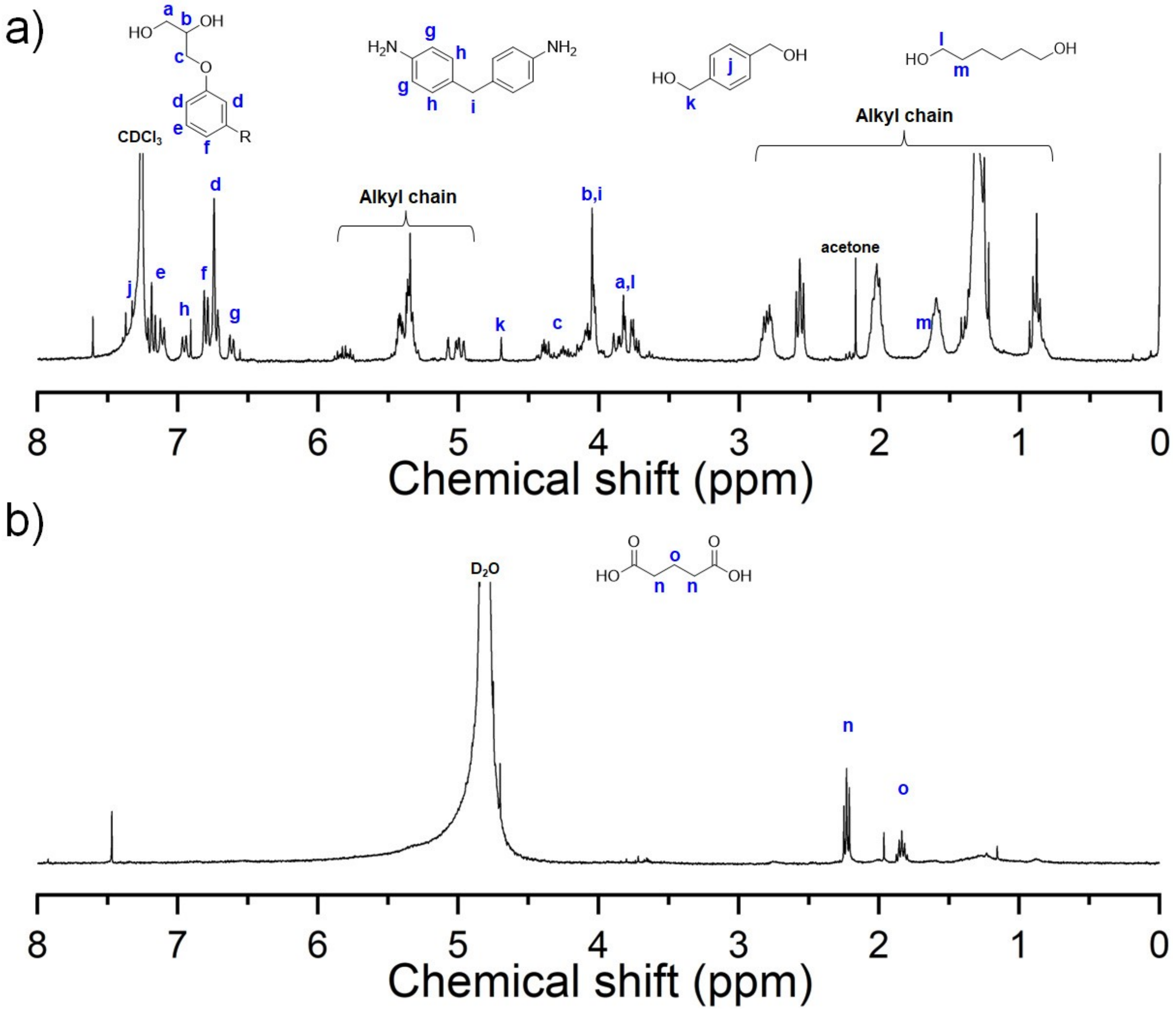

Figure S22. ^{1}H NMR spectra of PU-2 after 5 days of hydrolytic degradation conditions. (a) measured in $CDCl_3$, (b) measured in D_2O, showing the appearance of water-soluble degradation products such as glutaric acid.

Table S1. Summary of adhesion properties values of the synthesized polymers and commercial products.

PSA formulations		Adhesive performance	
Polymer	Tackifier (wt %)	Peel adhesion (N cm^{-1})	Tack (N)
PU-1	0	0.05	0.26 ± 0.08
PU-1.5	0	0.09 ± 0.01	1.19 ± 0.14
	20	0.12 ± 0.01	1.13 ± 0.16
	40	1.39 ± 0.21	1.21 ± 0.42
PU-2	0	3.17 ± 0.18	1.03 ± 0.24
	20	4.97 ± 0.75	0.78 ± 0.09
	40	5.69 ± 0.21	0.24 ± 0.06
PU-2.5	0	2.41 ± 0.39	0.7 ± 0.26
	20	4.27 ± 0.97	0.01
	40	4.75 ± 0.69	0.15 ± 0.13
PU-3	0	0.51 ± 0.1	0.01
	20	6.19 ± 0.48	0.12 ± 0.04
	40	5.55 ± 0.57	0.01
Sticky note[a]		< 0.04	0.14 ± 0.12
Office tape		1.9 ± 0.05	0.91 ± 0.05
Electric tape[a]		1.37 ± 0.12	2.58 ± 0.14

[a] Reported by Lee *et al.*[1]

References

1. S. Lee, K. Lee, Y.-W. Kim and J. Shin, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2309–2320.