Supporting Information

Thermally and base-triggered 'debond-on-demand' crosslinked polyurethane adhesives

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Materials

PTHF 2000 ($M_n = 2000 \text{ g mol}^{-1}$) was purchased from Sigma Aldrich and dried under a vacuum at 80 °C for 3 hours prior to use, 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI, Sigma Aldrich, 90.0%), 1,1,1-tris(hydroxymethyl)ethane (TMP, Sigma Aldrich, \geq 98.0%), and dibutyltin dilaurate (DBTDL, Sigma Aldrich, 95.0%) were used as received. 2,2'-Sulfonyldiethanol (SDE) was purchased from Fluorochem and dried by repeated azeotropic distillation *in vacuo* with ethanol and then dried over phosphorus pentoxide for 1 week prior to use. *Tetra*-butylammonium fluoride (TBAF, 97%) was purchased from Apollo scientific. Tetrahydrofuran (THF) was dried by using an MBRAUN SP7 system fitted with activated alumina columns.

Characterisation

Fourier-Transform Infrared (FT-IR) spectroscopic analysis was carried out at room temperature using a Perkin Elmer 100 FT-IR instrument equipped with a diamond-ATR sampling accessory. Thermogravimetric analysis (TGA) was carried out on TA Instruments TGA Q50 instrument with aluminium Tzero pans. The sample was heated from 20 °C to 600 °C at 10 °C min⁻¹ under nitrogen gas with a flow rate of 60 mL min⁻¹. Differential calorimetry (DSC) measurements were performed on a TA Instruments X3 DSC adapted with a TA Refrigerated Cooling System (RCS90), using aluminium TA Tzero pans and Hermetic lids, measuring from -80 °C to 200 °C with heating and cooling rates of 5 °C min⁻ ¹ under nitrogen gas with a flow rate of 50 mL min⁻¹. The thermal characterisation of the samples was processed using the TRIOS software (version 5.1.1). Rheological measurements were performed on a Malvern Panalytical Kinexus Lab+ instrument fitted with a Peltier plate cartridge and 8 mm parallel plate geometry and analysed using rSpace Kinexus v1.76.2398 software. Tensile tests were carried out using a Thümler Z3-X1200 tensometer at a rate of 10 mm min⁻¹ with a 1 kN load cell and analysed using THSSD-2019 software. Small-angle X-ray scattering (SAXS) and Wide-angle X-ray scattering (WAXS) experiments were performed on a Bruker Nanostar instrument. Samples were mounted in modified DSC pans equipped with Kapton™ windows and mounted in an MRI electrical heating unit for temperature control. Gel permeation chromatography (GPC) analysis was conducted on an Agilent Technologies 1260 Infinity system using HPLCgrade THF at a flow rate of 1.0 mL min⁻¹, calibration was achieved using a series of near monodisperse polystyrene standards.

General synthetic protocol for CEPUs (CEPU1-CEPU4) via one-pot (two-step) route.

A typical process to prepare **CEPU1** is described in the following text, and the rest of the CEPUs were prepared via same protocol with different molar ratios of 2,2'-sulfonyldiethanol (SDE) and 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) as shown in **Table 1**. Poly(tetrahydrofuran) (PTHF 2000), molecular weight (M_n = 2000 g mol⁻¹) was dried under a vacuum at 80 °C for 3 hr prior to use. In the bulk, PTHF 2000 (10.00 g, 5 mmol, 1.00 equiv.) and SDE (0.385 g, 2.5 mmol, 0.50 equiv.) were mixed with diisocyanate (HMDI) (3.30 g, 13 mmol, 2.50 equiv.) and dibutyltin dilaurate (DBTDL) (10 drops) at 80 °C under argon for 3 hr with gentle stirring. The colourless pre-polymer obtained was dissolved in dry THF (50 mL) and 1,1,1-tris(hydroxymethyl)ethane (TMP) (0.402 g, 3.35 mmol, 0.67 equiv.) was then added to the solution which was then held for another 10 min at 60 °C until the viscosity gradually increased. NCO:OH ratio of the final polymer solution is 1:1 and calculated from molar ratios in **Table 1**. The viscous polymer solution was poured into a 10 cm × 10 cm mould with a PTFE base and then put in an oven at 60 °C for further 18 hr; then under partial vacuum (approximately 600 mbar) at 60 °C for 24 hr, the polymer film was then allowed to reach room temperature before being removed from the mould and a transparent film was obtained, see Figure S1.

Synthesis of polymer CEPU1

The synthesis was carried out according to the general synthetic protocol described above for CEPUs; **CEPU1** was obtained as a colourless elastomeric solid (13.41 g, 92%). T_m = 18.84 °C, T_{cc} = -19.06, T_c = -26.64; FT-IR ATR (cm⁻¹): 3325 (vN-H_{stretch}), 2927 (vC-H_{alkyl}), 2850 (vC-H_{alkyl}), 2795 (vC-H_{alkyl}), 1712 (vC=O_{urethane}), 1701 (vC=O_{urethane}), 1530 (C-N_{stretch}), 1447 (vC-H_{alkyl}), 1366 (vC-H_{alkyl}), 1319 (vS=O_{stretch}).

Synthesis of polymer CEPU2

The synthesis was carried out according to the general synthetic protocol described above for CEPUs using PTHF 2000 (10.00 g, 5.00 mmol, 1 equiv.), SDE (0.769 g, 5 mmol, 1 equiv.), HMDI (3.93 g, 15.00 mmol, 3 equiv.), and TMP (0.401 g, 3.34 mmol, 0.667 equiv.); **CEPU2** was obtained as a colourless elastomeric solid (13.12 g, 90%). T_m = 19.03 °C, T_{cc} = -22.60, T_c = -28.55; FT-IR ATR (cm⁻¹): 3324 (vN-H_{stretch}), 2926 (vC-H_{alkyl}), 2850 (vC-H_{alkyl}), 2795 (vC-H_{alkyl}), 1710 (vC=O_{urethane}), 1700 (vC=O_{urethane}), 1530 (C-N_{stretch}), 1447 (vC-H_{alkyl}), 1366 (vC-H_{alkyl}), 1319 (vS=O_{stretch}).

Synthesis of polymer CEPU3

The synthesis was carried out according to the general synthetic protocol described above for CEPUs using (10.00 g, 5.00 mmol, 1 equiv.), SDE (1.15 g, 7.50 mmol, 1.5 equiv.), HMDI (4.60 g, 17.50 mmol, 3.5 equiv.), and TMP (0.401 g, 3.34 mmol, 0.667 equiv.);**CEPU3** was obtained as a colourless elastomeric solid (13.60 g, 94%). T_m = 19.75 °C, T_{cc} = -16.65, T_c = -26.38; FT-IR ATR (cm⁻¹): 3324 (vN-H_{stretch}), 2925 (vC-H_{alkyl}), 2850 (vC-H_{alkyl}), 2795 (vC-H_{alkyl}), 1699 (vC=O_{urethane}), 1529 (C-N_{stretch}), 1447 (vC-H_{alkyl}), 1366 (vC-H_{alkyl}), 1320 (vS=O_{stretch}).

Synthesis of polymer CEPU4

The synthesis was carried out according to the general synthetic protocol described above for CEPUs using PTHF 2000 (10.00 g, 5.00 mmol, 1 equiv.), SDE (1.55 g, 10.00 mmol, 2 equiv.), HMDI (5.23 g, 20.00 mmol, 4 equiv.), and TMP (0.401 g, 3.34 mmol, 0.667 equiv.);**CEPU4** was obtained as a colourless elastomeric solid (13.57 g, 95%). T_m = 20.10 °C, T_{cc} = -18.00, T_c = -33.12; FT-IR ATR (cm⁻¹): 3327 (vN-H_{stretch}), 2925 (vC-H_{alkyl}), 2850 (vC-H_{alkyl}), 2795 (vC-H_{alkyl}), 1699 (vC=O_{urethane}), 1529 (C-N_{stretch}), 1447 (vC-H_{alkyl}), 1366 (vC-H_{alkyl}), 1320 (vS=O_{stretch}).



Figure S1: Representative homogeneous cast films (10 cm × 10 cm × 1 mm) of (**A**) **CEPU1**, (**B**) **CEPU2**, (**C**) **CEPU3**, and (**D**) **CEPU4** in aluminium moulds.



Figure S2. (**A**) the FT-IR spectrum of **CEPU1-CEPU4**, (**B**) increases the intensity of the absorption bands for the N-H group, and (**C**) increase the intensity of the absorption bands for the urethane and sulfone groups from **CEPU1-CEPU4**.



Figure S3. TGA thermogram of CEPU1 at 10 °C min⁻¹ under nitrogen.



Figure S4. TGA thermogram of CEPU2 at 10 °C min⁻¹ under nitrogen.



Figure S5. TGA thermogram of CEPU3 at 10 °C min⁻¹ under nitrogen.



Figure S6. TGA thermogram of CEPU4 at 10 °C min⁻¹ under nitrogen.



Figure S7. DSC thermogram of **CEPU1** showing (**A**) the 1st heating after isotherm at -90 °C for 60 min, and (**B**) the 1st, 2nd, and 3rd heating and cooling cycles at 10 °C min⁻¹.



Figure S8. DSC thermogram of **CEPU2** showing (**A**) the 1st heating after isotherm at -90 °C for 60 min, and (**B**) the 1st, 2nd, and 3rd heating and cooling cycles at 10 °C min⁻¹.



Figure S9. DSC thermogram of **CEPU3** showing (**A**) the 1st heating after isotherm at -90 °C for 60 min, and (**B**) the 1st, 2nd, and 3rd heating and cooling cycles at 10 °C min⁻¹.



Figure S10. DSC thermogram of **CEPU4** showing (**A**) the 1st heating after isotherm at - 90 °C for 60 min, and (**B**) the 1st, 2nd, and 3rd heating and cooling cycles at 10 °C min⁻¹.



Figure S11. Temperature sweep analysis of **CEPU1** (A), **CEPU2** (B), **CEPU3** (C), and (D) **CEPU4**, using a normal force of 1 N and a frequency of 1 Hz.



Figure 12. SAXS profiles of CEPU1-CEPU4 at 25 °C.

CEPU	<i>q</i> _{max} (nm ⁻¹)	<i>d</i> -spacing (nm)
CEPU1	0.52	11.99
CEPU2	0.90	6.91
CEPU3	1.69	3.70
CEPU4	2.99	2.09

Table S1. q_{max} and corresponding *d*-spacing for **CEPU1-CEPU4** at 25 °C.



Figure S13. VT-SAXS and VT-WAXS profiles of **CEPU2** (**A** and **B**, respectively) and **CEPU3** (**C** and **D**, respectively) as a function of temperature, recorded at 25 °C intervals from 25°C to 200 °C at a heating rate of 25 °C min⁻¹.



Figure S14. Comparison of ultimate tensile strength and elongation at break for **CEPU4** with examples of cross-linked polyurethanes adhesives reported in the literature.¹⁻¹¹

	Ultimate Tensile	Young's	Modulus of	Elongation
CEF US	Strength (MPa)	modulus (MPa)	toughness (MJm ⁻³)	at break (ε)
CEPU1	9.64 ± 0.21	4.57 ± 1.31	29.56 ± 7.67	8.63 ± 0.26
	31.04 ± 0.31	9.33 ± 1.53	221.94 ± 9.51	14.96 ±
CEPUZ				0.41
	41.14 ± 0.44	20.21 ± 0.85	308.45 ± 11.65	16.11 ±
GEFU3				0.50
CEDIIA	42.68 ± 0.71	49.04 ± 1.10	360.72 ± 10.83	17.59 ±
CEPU4				0.94

Table S2: Mechanical properties of **CEPU1-CEPU4**, (errors shown are standard deviations, values shown are the average of 3 repeats for each sample).

Table S3. Representative adhesions cycles of CEPUs on glass, aluminium, and Nylon 6,6, over five re-adhesion cycles (30 min/cycle at 150 °C). The error shown is the standard deviation between the three repeats for each sample.

CEPUs	Glass Shear Strength (MPa)					
adhesive	Cycle 0	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
CEDIII	3.72 ±	3.65 ±	3.30 ±	3.64 ±	3.39 ±	2.76 ±
CEPUI	0.11	0.81	0.12	0.11	0.15	0.27
CEDU2	4.64 ±	4.48 ±	4.07 ±	4.76 ±	4.73 ±	3.97 ±
GEFUZ	0.82	0.39	0.31	0.16	0.78	0.03
CEDUS	5.39 ±	5.30 ±	6.16 ±	5.21 ±	4.88 ±	4.9 ±
	0.15	0.30	0.80	0.42	0.29	0.08
СЕРНИ	6.04 ±	6.01 ±	6.05	5.23 ±	5.23 ±	5.22 ±
	0.21	0.37	±0.24	0.30	0.07	0.04
	Alum	inium Shear	Strength (M	IPa)		
	Cycle 0	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
CEDIIA	3.58 ±	2.48 ±	2.06 ±	4.53 ±	4.43 ±	4.03 ±
CEPUI	0.69	0.48	0.40	0.21	0.63	0.48
CEDII2	5.84 ±	5.53 ±	4.96 ±	4.91 ±	5.13 ±	5.13 ±
	0.53	0.53	0.19	0.42	0.32	0.16
CEPUS	6.96 ±	6.93 ±	6.87 ±	6.84 ±	5.80 ±	5.49 ±
	0.06	0.60	0.25	0.41	0.12	0.02
CEPI14	7.80 ±	7.71 ±	7.61 ±	7.61 ±	7.26 ±	7.26 ±
	0.45	0.64	0.46	0.53	0.06	0.06
-	Nylon 6,6 Shear Strength (MPa)					
	Cycle 0	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
CEDIII	1.19 ±	1.72 ±	3.12 ±	2.90 ±	2.60 ±	2.71 ±
CLFUT	0.08	0.14	0.19	0.22	0.16	0.11
CEDII2	1.62 ±	2.23 ±	4.37 ±	4.16 ±	2.77 ±	2.77 ±
CLF UZ	0.16	0.02	0.13	0.14	0.19	0.22
CEPUS	2.40 ±	4.39 ±	4.28 ±	3.57 ±	2.89 ±	2.89 ±
ULF UJ	0.05	0.44	0.21	0.09	0.03	0.11
CEPU4	3.07 ±	4.57 ±	4.28 ±	3.35 ±	3.31 ±	3.34 ±
	0.16	0.09	0.01	0.20	0.04	0.05

Table S4. Representative adhesions of CEPUs on glass, aluminium, and Nylon 6,6 for 2.5 hr at 150 °C. The error shown is the standard deviation between the three repeats for each sample.

CEPUs	Glass Shear Strength (MPa)			
adhesive	Glass	Aluminium	Nylon 6,6	
CEDUI	4.02 ±	6.11 ±	3.83 ±	
CEPUI	0.31	0.15	0.21	
CEPU2	4.40 ±	6.45 ±	3.65 ±	
	0.08	0.33	0.19	
CEDU2	2.50 ±	7.60 ±	4.54 ±	
CEPU3	0.14	0.09	0.22	
CEDIIA	2.06 ±	8.27 ±	4.13 ±	
CEPU4	0.05	0.24	0.08	

Table S5. Comparison of **CEPU4** *vs.* literature cross-linked debond-on-demand adhesivesand debonding methods.

Substrate	Stimuli	Debonding Chemistry	Conditions	Reference
Aluminium, glass, and Nylon 6,6 substrates	Chemical	Thermal and base debonding of cross- linked polyurethane	1 M TBAF (aq), 30 minutes, room temperature	This work
Aluminium	Chemical	Debonding of backbone and reduction in crosslink density	0.025 M TBAF/acetonitrile, 40 °C, 3 h	12
PU foam/PET textile, PET foil/PET textile, and wood	Chemical	Depolymerization of backbone and reduction in crosslink density by acetal hydrolysis	1 M H₃PO₄, 1 M citric acid, or 1 M HCl, 80 °C,	13
Wood	Thermal	Thermally expandable particles and retro- Diels Alder	150 °C	14
Glass, PS, and PET	Chemical	Base debonding of cross-linked polymer	1 M CsF, methanol, room temperature	15
Aluminium	Chemical	Base debonding of cross-link silyl-PU networks.	1.0 M TBAF, THF, room temperature	5
Aluminium, PC, and wood	Thermal	Dissociative Diels– Alder	23 - 80 °C	16
Aluminium	Thermal	Retro-Diels-Alder	150 °C	17
Glass	Thermal, magnetic	Magnetic Fe ₃ O ₄ particles	Heat, 30 s - 5 min	18
Glass	Light	Isomerization (open and closed ring)	525 nm VIS light, 6 h	19



Figure S15. (**A**, **D**, **G**, **J**) FT-IR spectrum of **CEPU1** to **CEPU4**, respectively, at 25 °C and after adhesion for 2.5 hr at 150 °C on glass substrate, (**B**, **E**, **H**, **K**) absorption bands of the urethane and sulfone groups, and (**C**, **F**, **I**, **L**) absorption bands of the N-H group.



Figure S16. GPC eluogram of (A) **CEPU2** and (B) **CEPU3** in THF after 30 min, 6, 24, 30, 48, 54, and 72 hr post addition of TBAF (1 M).

CEPUs			<i>M_n</i> (g mc	ol ⁻¹)			
adhesive	30 min	6 hr	24 hr	30 hr	48 hr	54 hr	72 hr
CEPU1	9266 ±	9948 ±	11163 ±	10714	13865	13965	13681 ±
	258	461	327	± 261	± 20	± 226	315
CEPU2	6393 ±	7131 ±	7587 ±	7768 ±	9124 ±	11290	10471 ±
	65	300	86	112	778	± 691	62
CEPU3	4745 ±	6326 ±	6472 ±	5753 ±	8183 ±	8347 ±	8415 ±
	214	88	48	626	276	94	103
CEPU4	4479 ±	5579 ±	5843 ±	6379 ±	6944 ±	7306 ±	7367 ±
	81	90	95	309	52	41	21
			<i>M</i> _w (g mo	ol⁻¹)			
	30 min	6 hr	24 hr	30 hr	48 hr	54 hr	72 hr
CEPU1	26671 ±	30809 ±	36262 ±	44288	55697	53286	53195 ±
	74	91	523	± 1781	± 740	± 142	2123
CEPU2	16493 ±	18812 ±	21607 ±	31208	37534	36704	34326 ±
	120	383	274	± 1885	± 2229	± 1484	2461
CEPU3	11505 ±	13554 ±	13780 ±	18009	24467	21554	19443 ±
	278	77	119	± 2220	± 593	± 492	92
CEPU4	10292 ±	11869 ±	11836 ±	17369	18553	15985	15798 ±
	107	140	63	± 320	± 336	± 116	130
			Ð				
	30 min	6 hr	24 hr	30 hr	48 hr	54 hr	72 hr
CEPU1	2.88 ±	3.11 ±	3.26 ±	4.13 ±	4.02 ±	3.82 ±	3.89 ±
	0.07	0.13	0.14	0.07	0.05	0.05	0.06
CEPU2	2.58 ±	2.65 ±	2.85 ±	4.03 ±	4.15 ±	3.26 ±	3.14 ±
	0.01	0.12	0.07	0.30	0.14	0.07	0.25
CEPU3	2.43 ±	2.14 ±	2.13 ±	3.11 ±	2.99 ±	2.58 ±	2.31 ±
	0.05	0.02	0.03	0.09	0.05	0.06	0.03
CEPU4	2.30 ±	2.13 ±	2.03 ±	2.73 ±	2.67 ±	2.19 ±	2.14 ±
	0.02	0.05	0.03	0.08	0.06	0.02	0.02

Table S6. GPC molecular weight and dispersity data of **CEPU1-CEPU4** in THF after 30 min, 6, 24, 30, 48, 54, and 72 hr post addition of TBAF (1 M). The error shown is the standard deviation between the three repeats of each sample.

Table S7. Shear strength of **CEPU4** on aluminium, glass, and Nylon 6,6 after exposure to $1 \text{ M TBAF}_{(aq)}$ for 30 min; the order of the data in the table for each entry is as follows: shear strength; % loss in shear strength. The error shown is the standard deviation between the three repeats of each sample. The percentage error shown is the standard error between the pristine and degraded averages for each sample.

CEPU adhesive	Substrate	Pristine shear strength (MPa)	Degraded shear strength (MPa)
CEPU4	Aluminium	7.71 ± 0.64 -	5.11 ± 0.12 34 ± 18%
CEPU4	Glass	6.04 ± 0.21 -	4.17 ± 0.17 31 ± 8%
CEPU4	Nylon 6,6	3.07 ± 0.16 -	2.64 ± 0.11 14 ± 6%

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