Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A Dynamic Polyurea Network with Exceptional Creep Resistance

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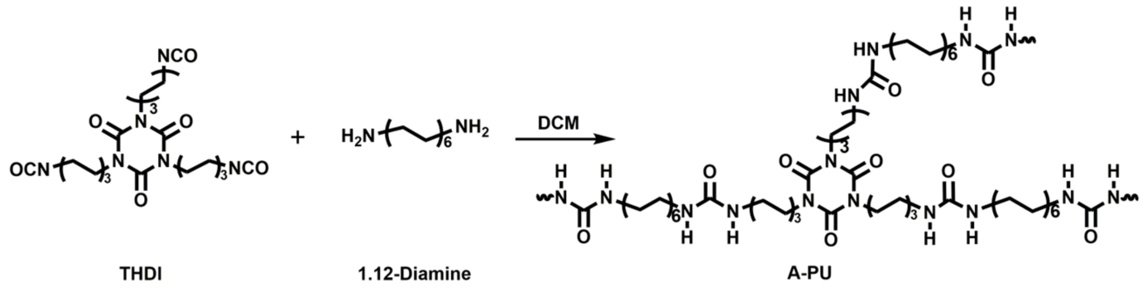
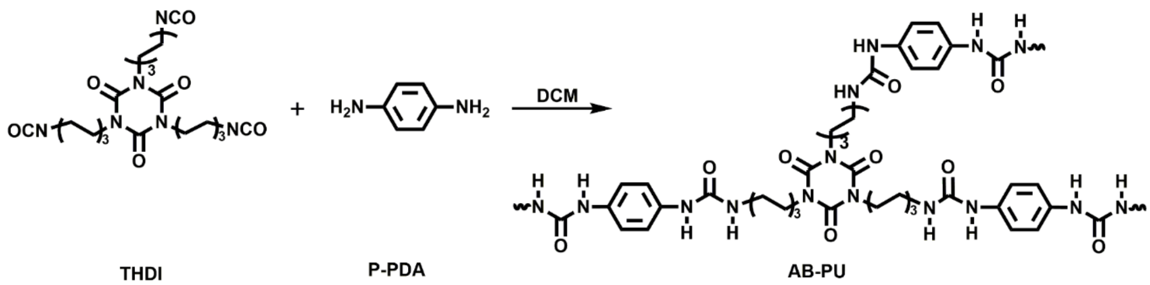
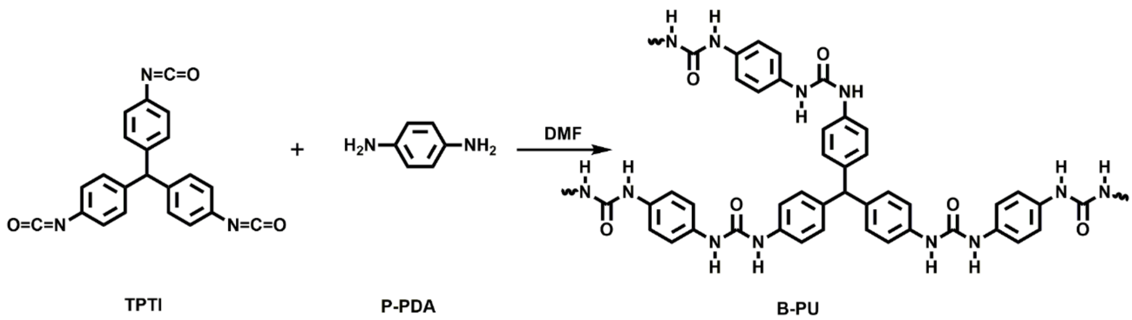
1. Preparation of A-PU$_x$, AB-PU$_{1.2}$ and B-PU$_{1.2}$



Scheme S1. Synthesis route of A-PU$_x$.



Scheme S2. Synthesis route of AB-PU$_{1.2}$.



Scheme S3. Synthesis route of B-PU$_{1.2}$.

2. Results and discussions

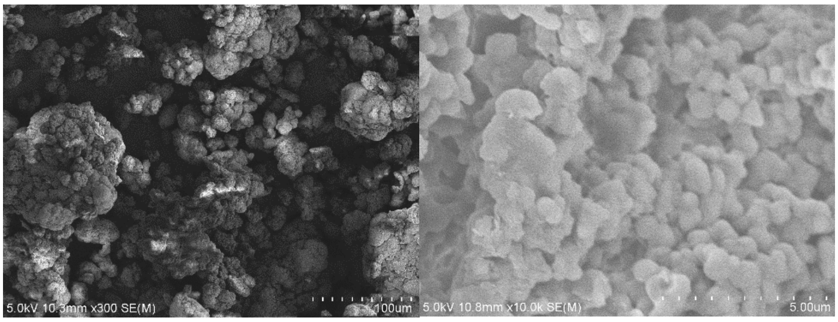


Fig. S1 SEM images of raw products of A-$PU_{1.2}$.

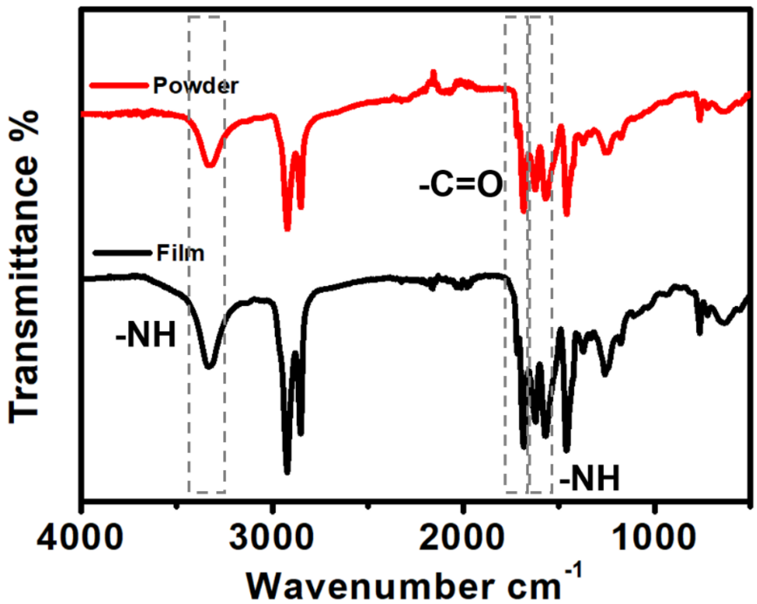


Fig. S2 FT-IR spectra of white powder and film of A-$PU_{1.2}$.

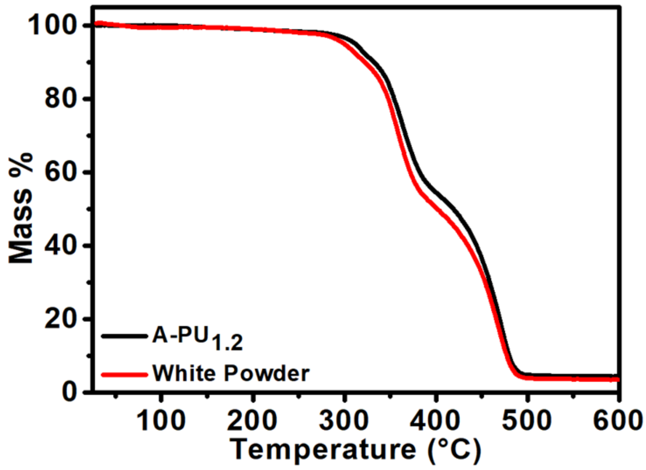


Fig. S3 TGA curves of A-$PU_{1.2}$ film and white powder heated from 30 to 600 °C.

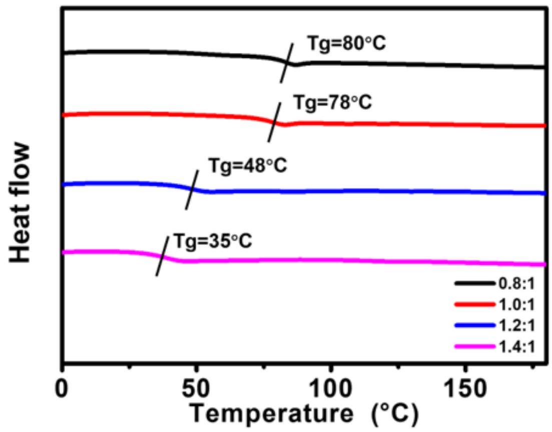


Fig. S4 DSC curves of four samples with different ratios.

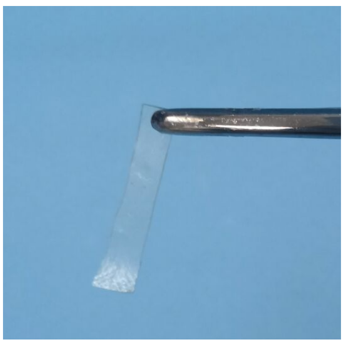


Fig. S5 The optical image of A-$PU_{1.2}$ after tensile test.

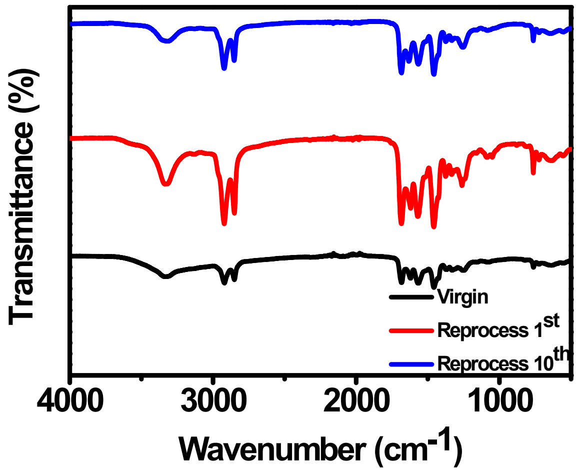


Fig. S6 FT-IR curves of A-PU$_{1.2}$ after multiple cycles of reprocess.

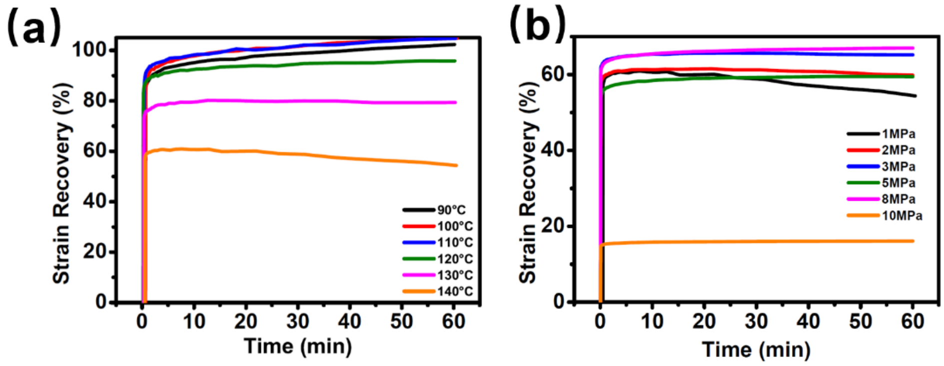


Fig. S7 Creep recovery curves of A-PU$_{1.2}$ (a) at different temperatures after exposure to 1 MPa, (b) at 140 °C under different levels of stresses.

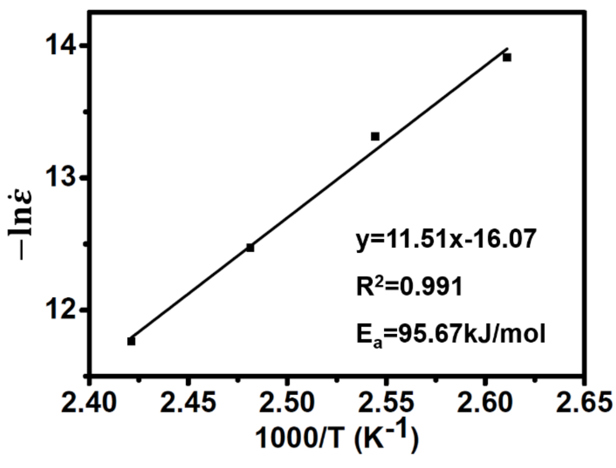


Fig. S8 Arrhenius fitting plot of the A-PU$_{1.2}$ obtained from creep experiments.

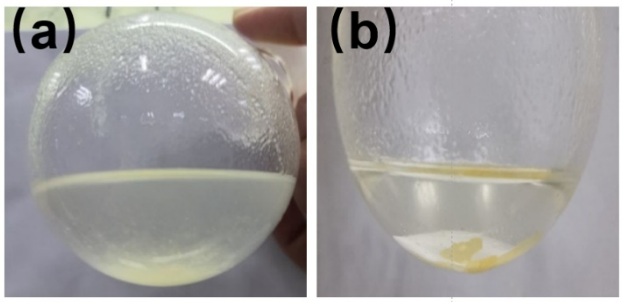


Fig. S9 The state of (a) A-$PU_{1.2}$ white powder and (b) film fragments in NMP at 150 °C.

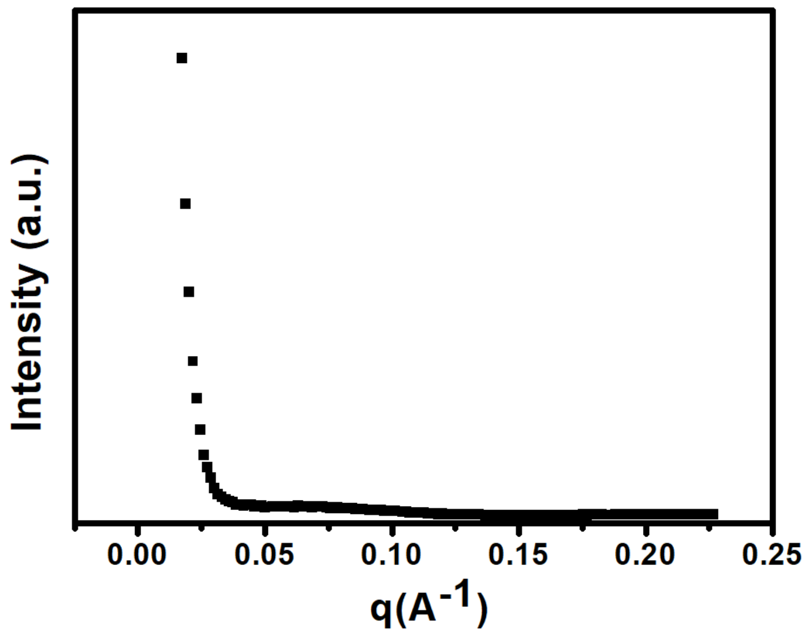


Fig. S10 The SAXS spectrum of A-$PU_{1.2}$. No peak characteristic was observed in this spectrum, indicating that there is no obvious phase separation in A-$PU_{1.2}$.

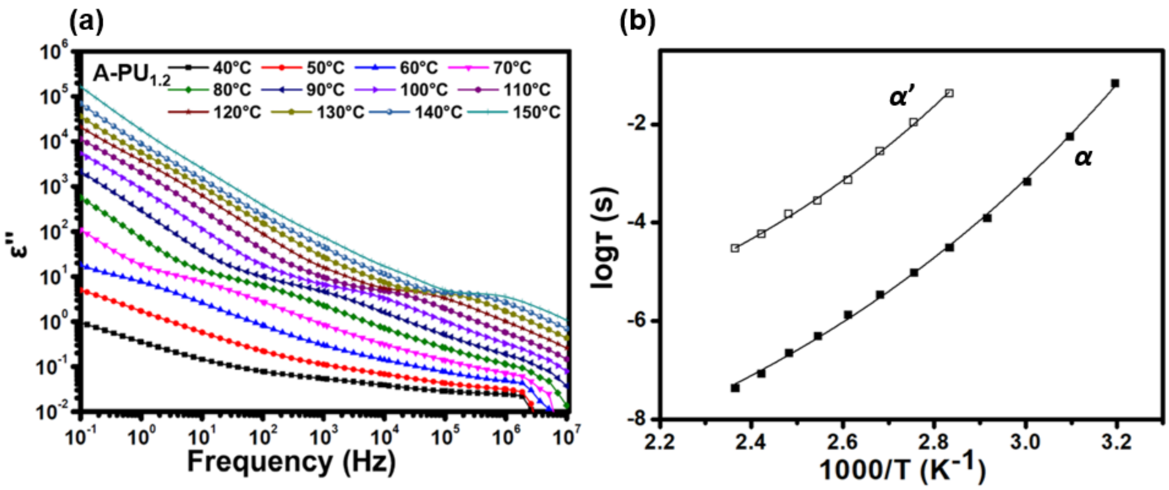


Fig. S11 Dielectric relaxation behavior of A-$PU_{1.2}$ above T_g. (a) Dielectric loss ε'' as a function of frequency for A-$PU_{1.2}$. (b) Average relaxation time as a function of temperature for α and α' relaxation process in A-$PU_{1.2}$. Solid lines represent VFT fitting.

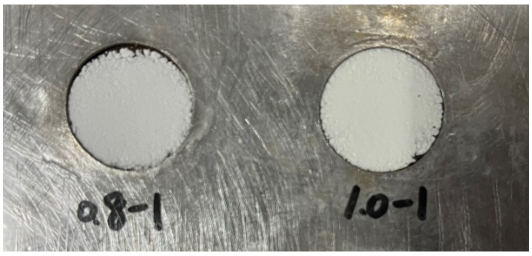


Fig. S12 The optical images of A-$PU_{0.8}$ and A-$PU_{1.0}$ after hot pressing of 140 °C and 1 MPa for 30 minutes.

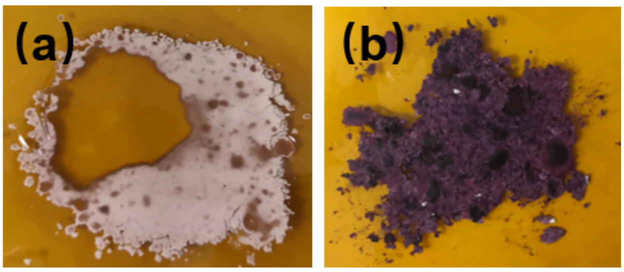


Fig. S13 The optical images of (a) AB-$PU_{1.2}$ and (b) B-$PU_{1.2}$ after hot press of 180 °C and 2 MPa for 2 hours.

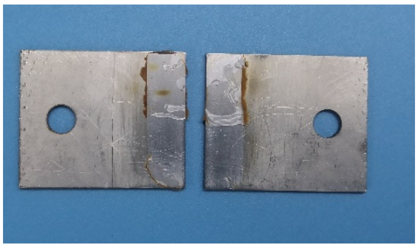


Fig. S14 The optical image of fracture surface of A-$PU_{1.2}$ adhesive.

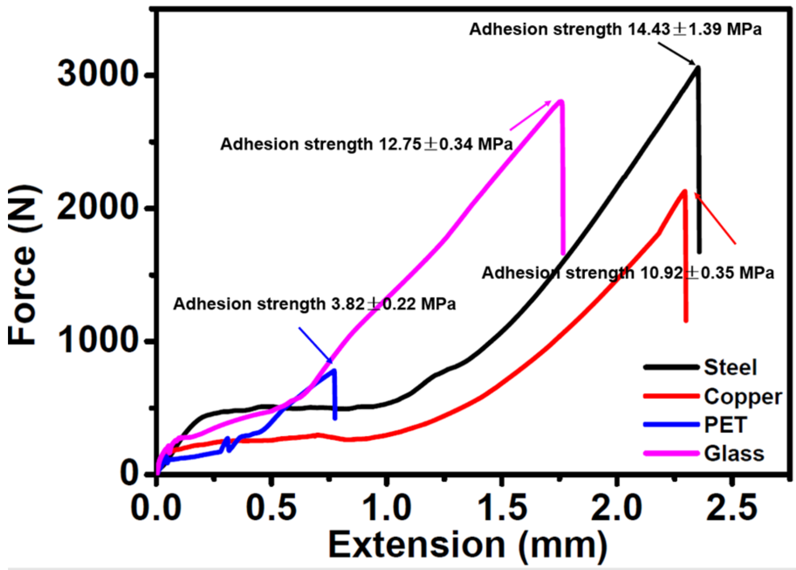


Fig. S15 The force-versus extension curves for steel, copper, PET and glass sheets adhered by A-$PU_{1.2}$ to show adhesion strength.

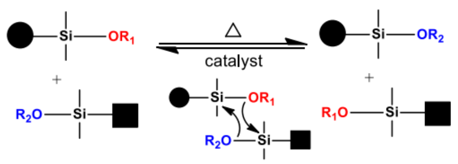
Table S1. Mechanical properties of A-PU$_{1.2}$ under different hot press temperature.

Hot press temperature (°C)	Strength (MPa)	Young's Modulus (MPa)	Elongation (%)	Toughness (MJ/m^3)
120	13.44	349.13	5.2	0.39
130	13.54	206.27	12.1	1.04
140	26.66	188.27	132.2	36.33
150	31.84	231.86	144.5	48.97
160	47.79	353.93	208.2	89.04

Table S2. Creep rate $\dot{\varepsilon}$ of A-PU$_{1.2}$ at different temperatures under a stress of 1MPa.

Temperature (°C)	Creep rate $\dot{\varepsilon}$ (%•s^{-1})
90	$1.45*10^{-6}$
100	$1.25*10^{-6}$
110	$9.09*10^{-7}$
120	$1.65*10^{-6}$
130	$3.83*10^{-6}$
140	$7.78*10^{-6}$

Table S3. The comparison of creep behavior of recyclable CANs reported previously.

Ref.	Dynamic motifs	Temperature (°C)	Stress (MPa)	Strain(%)
12	silyl ether metathesis 	140	0.1	80
24	S,O-thioacetal	140	1	3
25	β-carbonyl carboxylate	140	6	6
28	bis(2,2,6,6-tetramethylpiperidin-1-yl) disulfide methacrylate (BiTEMPS methacrylate)	70	0.01	8

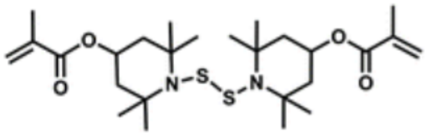
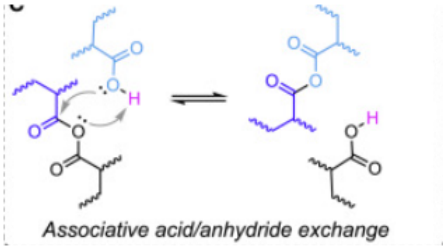
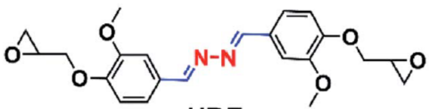
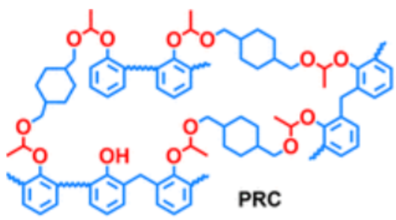
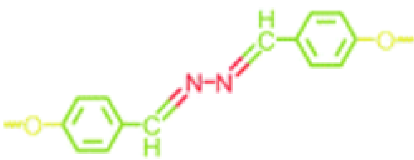
	 BiTEMPS methacrylate			
29	Polyimine-metal complex	140	1	3.5
31	acid-anhydride bond exchange 	100	0.005	3.5
32	vinylogous urethane (block vitrimer) 	140	0.005	0.6
36	Dihydrazone  HBE	150	1	10
38	silyl ether	80	0.002	1.75
39	asymmetric acetal 	120	1	9
40	Azine 	140	1	65
41	Hinded urea bonds	150	0.05	17

Table S4. Swelling ratio of A-$PU_{1.2}$ in various solvents for a month.

Solvent	Swelling ratio (%)
DMF	114.65
THF	118.21
MeCN	103.82
DMSO	106.46
NaOH	104.76
H_2O	103.54
Tol	115.07
DMAc	122.95
CH_3OH	114.57
EtOH	114.55
HCl	102.21
1% H_2O_2	102.54

Movie S1. The joints adhered by A-$PU_{1.2}$ can bear a load of 80 kg at room temperature.