Mechanically robust, creep resistant, intrinsic antibacterial and reprocessable dynamic polyurethane networks based on Azine moiety

Jinshi Han, Yawei Zhou, Guanghang Bai, Wei Wei, Xiaoya Liu,* and Xiaojie Li*

Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, No 1800 Lihu Avenue, Wuxi, Jiangsu, 214122, P. R. China.

E-mail: xjli@jiangnan.edu.cn, lxy@jiangnan.edu.cn

Gel and swelling measurement

The gel fraction and swelling ratio of samples were determined at room temperature by immersing the samples in DMF for three days with the DMF refreshed each day. After that, the insoluble polymer was dried at 100 °C under vacuum to the constant weight (W_2). The original weight of the sample was expressed as W_0. The weight of the swollen sample immediately taken out of DMF and wiped surface up with tissues was signed as $W1$. Therefore, the gel fraction (GF) and the swelling ratio (SR) were calculated according to the following formulas: $GF = W_2/W_0$; $SR = (W_1-W_0)/W_0$.

Dynamic depolymerization and repolymerization of linear ACPCN

IPDI (8 mmol), PTMEG (4 mmol) and HEBAA (4 mmol) were stirred in dry DMF (16.5 g) at 60 °C for 16 h to form the solution of linear ACPCN. A little aliquot was taken to test molecular weight by GPC. Then additional HEBAA (4 mmol) was added and the solution was heated to higher temperature (150 °C). After 6 hours, the reaction was cooled to 60 °C and one aliquot was taken for GPC experiment. Finally, additional IPDI (4 mmol) was added to the solution. After 16 h reaction at 60 °C, one aliquot was taken for GPC experiment.

Reprocessing recycling of Azine-containing Polyurethane (ACPCN)

The ACPCN41151 was cut into pieces and placed into a rectangular metal mould (ca. 60 mm (L) × 40 mm (W) ×0.5 (T)). The mould was laminated by two polyimide films and hot pressed under ~10 MPa at 150 °C in a plate vulcanizer for 20 min. The reprocessed film was cooled to room temperature by cold water and demolded.

Determination of cross-linking density (v) and molecular weight between cross-links (M_c)

The cross-linking density (v) and molecular weight between cross-links (M_c) were evaluated by the equation (S1):

$$E = 3vRT = \frac{3\rho RT}{M_c} \qquad\qquad (S1)$$

Where E is tensile storage modulus measured at 100 °C by DMA, ρ is the density of ACPCN, R is the gas constant 8.314 J/mol·K and T refers to the absolute temperature (373 K).

Determination of relaxation time (τ^*) and exchange activation energy (E_a)

The relaxation time (τ^*) is defined from the Maxwell model of viscoelastic fluids as the time required for the relaxation modulus (G) to fall to e^{-1} (~37%) of the initial relaxation modulus (G_0). The relationship of the relaxation time τ^* and Activation energy of the exchange reaction (E_a) was expressed by Arrhenius equation (equation S2):

$$\tau^*(T) = \tau_0 exp\left(\frac{E_a}{RT}\right) \qquad (S2)$$

Where $\tau^*(T)$ is the relaxation time at actual temperature, τ_0 is the characteristic relaxation time at infinite temperature, E_a is the relaxation activation energy (kJ·mol^{-1}), R is the universal gas constant and T (K) is the absolute temperature at which the stress relaxation is performed.

Taking the natural logarithm of the Arrhenius equation and rearranging the terms yields an equation that has the same form as the equation (S3) of a straight line with a slope of $E_a/1000R$:

$$ln\tau^*(T) = ln\tau_0 + \frac{E_a}{1000R} \cdot \frac{1000}{T} \qquad (S3)$$

By plugging the relaxation time and temperature acquired from stress relaxation analysis into equation (3), a fitted line could be obtained for each sample (Figure 3d and Figure S4b, S5b, S6b). E_a could be calculated from the slope.

**Calculation of Freezing-transition temperature (T_v):**

The polymer network topology was regarded as a viscoelastic liquid and its viscosity was 10^{12} Pa·s at topology freezing transition temperature (T_v)[1, 2]. The relationship of viscosity and relaxation time could be determined by Maxwell equation (equation S4)[3, 4]:

$$\eta = \frac{E \cdot \tau^*}{3} \qquad (S4)$$

Where E is tensile storage modulus measured at 100 °C by DMA，τ^* is the relaxation time. The viscosity was 10^{12} Pa·s at T_v and τ^* could be calculated using equation S4. Then, this τ^* was plugged to the fitted linear equation and T_v could be calculated.

Antibacterial test

The antibacterial activities of ACPCN41151 and control sample were studied against Escherichia coli (E. coli, Gram-negative) and Staphylococcus aureus (S. aureus, Gram-positive) by the plate counting method. E. coli or S. aureus (20 μL) was seeded into the LB nutrient solution (20 mL), which was shook in the constant temperature incubator at 37 °C for 12 h. The concentration was diluted to 10^5-10^6 CFU/mL. The sterilized specimens were immersed in the nutrient solution and cultured in the constant temperature incubator for 24 h at 37 °C. After incubation, both the samples were washed 3 times with 0.9% sodium chloride solution to remove the non-adhered bacteria. The samples were sonicated in the 0.9% sodium chloride solution for 30 min to release the adhered bacterial cells. Then, 100 μL sonicated bacterial suspension was diluted 100 times. Finally, 100 μL bacterial suspension was coated on the agar plate, which was incubated at 37 °C for 24 h followed by taking photographs.
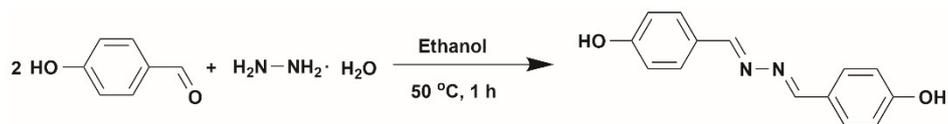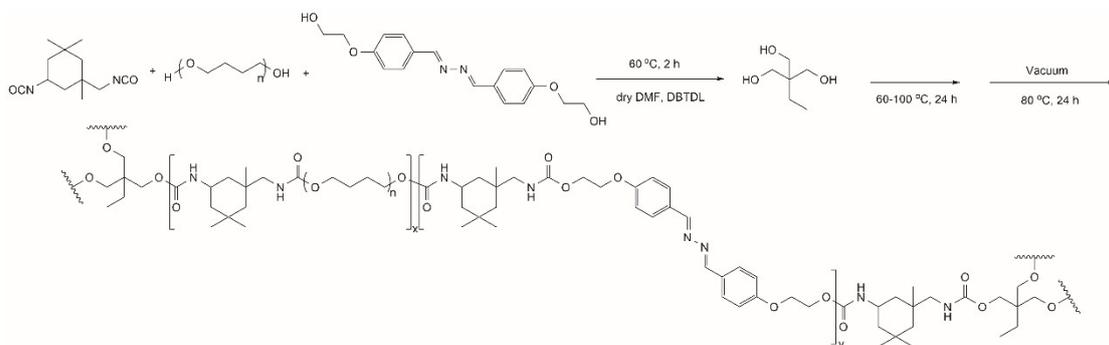
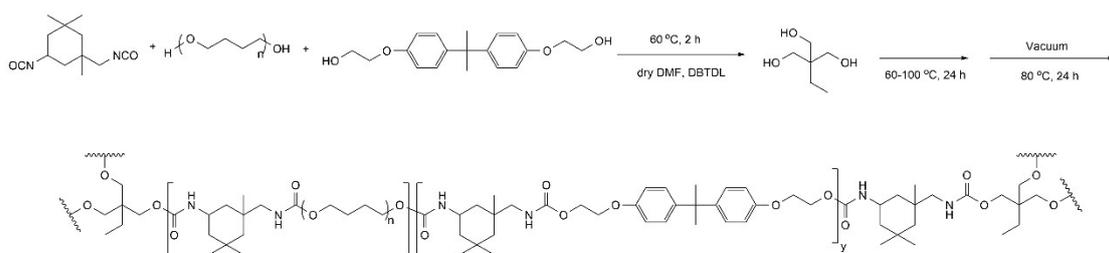**Scheme S1** Synthesis of p-Hydroxyl Benzaldehyde Azine (HBAA)

Scheme S2 Synthesis of p-Hydroxyethoxyl Benzaldehyde Azine (HEBAA)
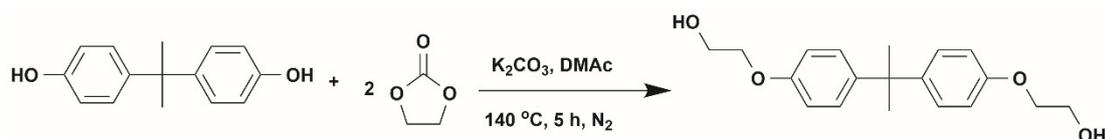
Scheme S3 Synthesis of Dihydroxyethoxyl Bisphenol A (DHEBPA)

Scheme S4 Preparation of Azine-containing Polyurethane Cross-linking Networks
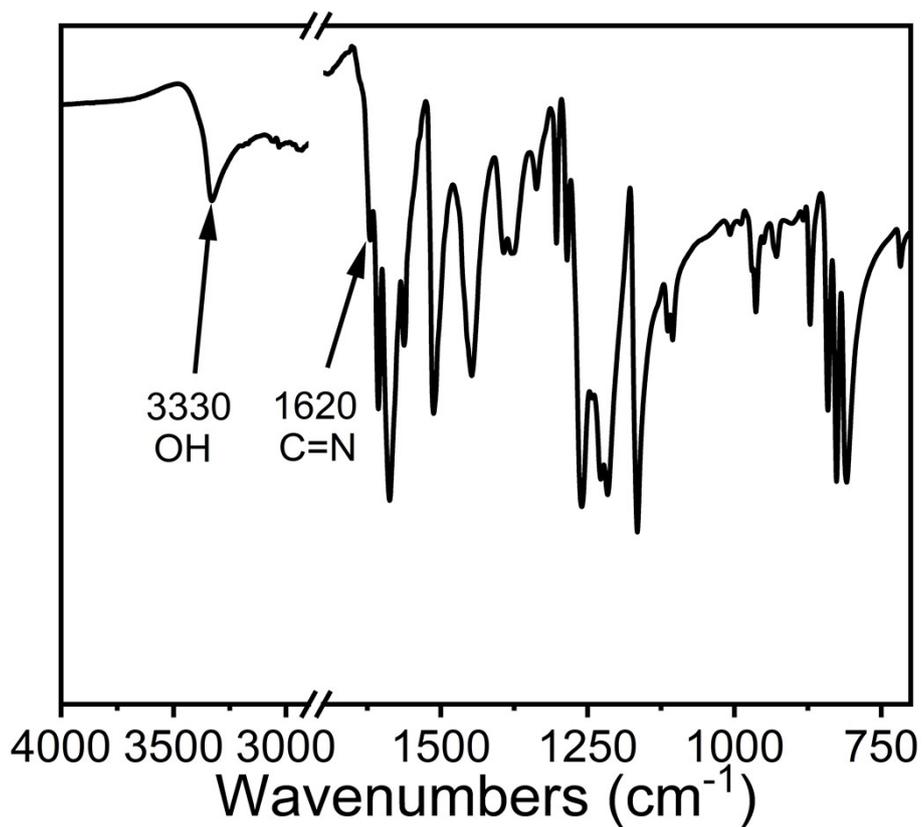

Scheme S5 Preparation of the control sample
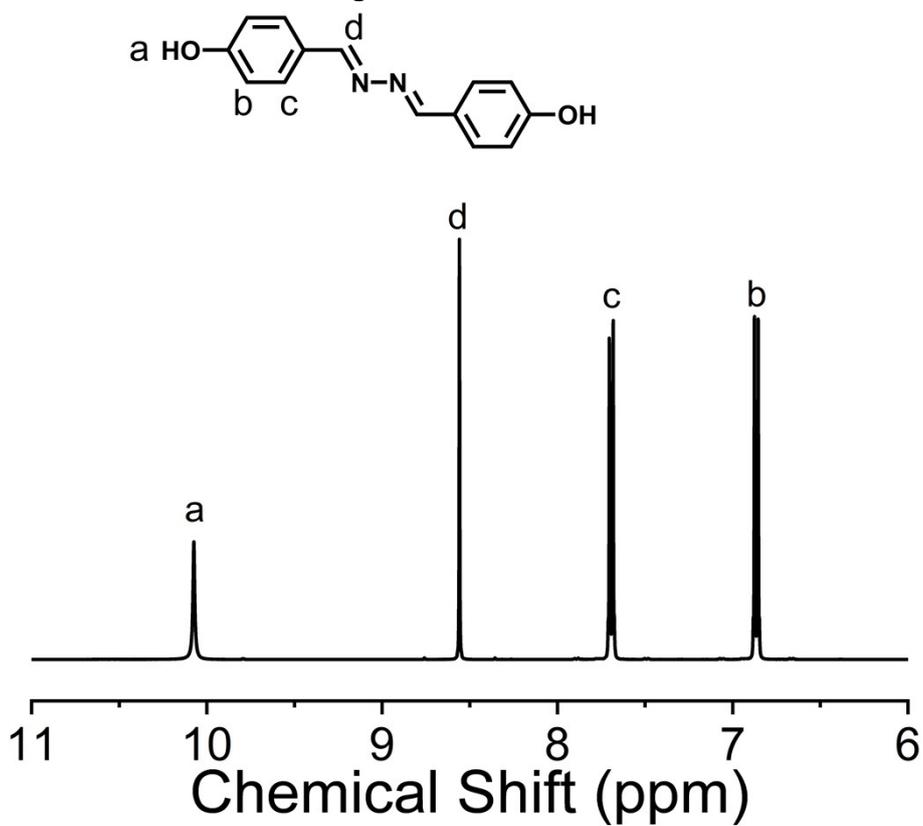
Fig. S1 FTIR of HBAA
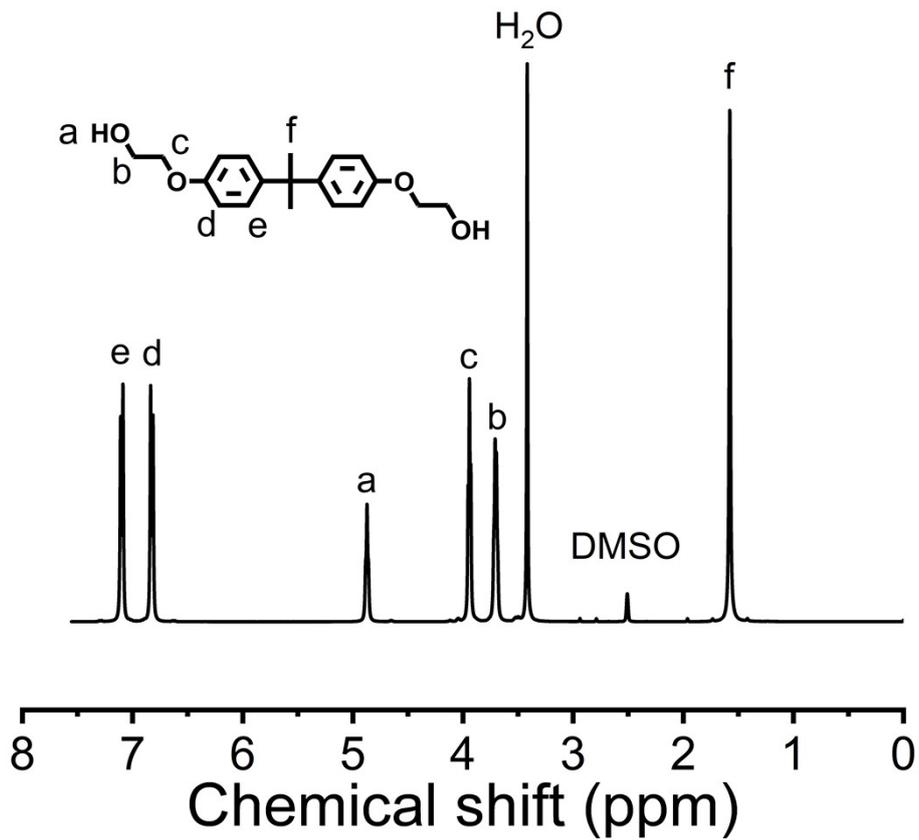

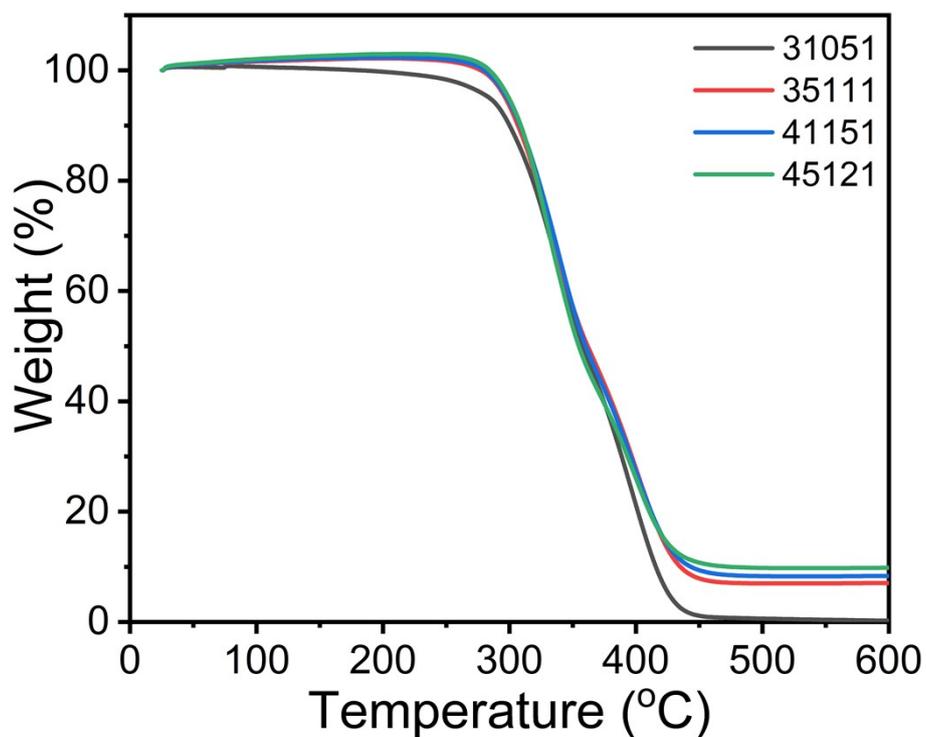**Fig. S2** ^{1}HNMR of HBAA

Fig. S3 ^{1}HNMR of DHEBPA

Fig. S4 TGA of ACPCNs

Fig. S5 (a) Stress relaxation of ACPCN31051 measured at various temperature. (b) the fitted line derived from characteristic relaxation time versus 1000/T and relaxation activation energy of ACPCN31051
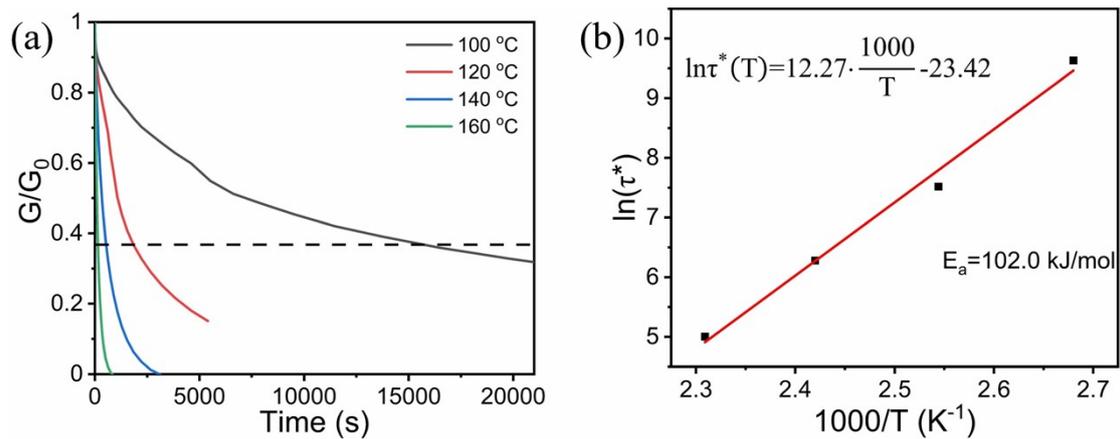

Fig. S6 (a) Stress relaxation of ACPCN35111 measured at various temperature. (b) the fitted line derived from characteristic relaxation time versus 1000/T and relaxation activation energy of ACPCN35111

Fig. S7 (a) Stress relaxation of ACPCN45121 measured at various temperature. (b) the fitted line derived from characteristic relaxation time versus 1000/T and relaxation activation energy of ACPCN45121
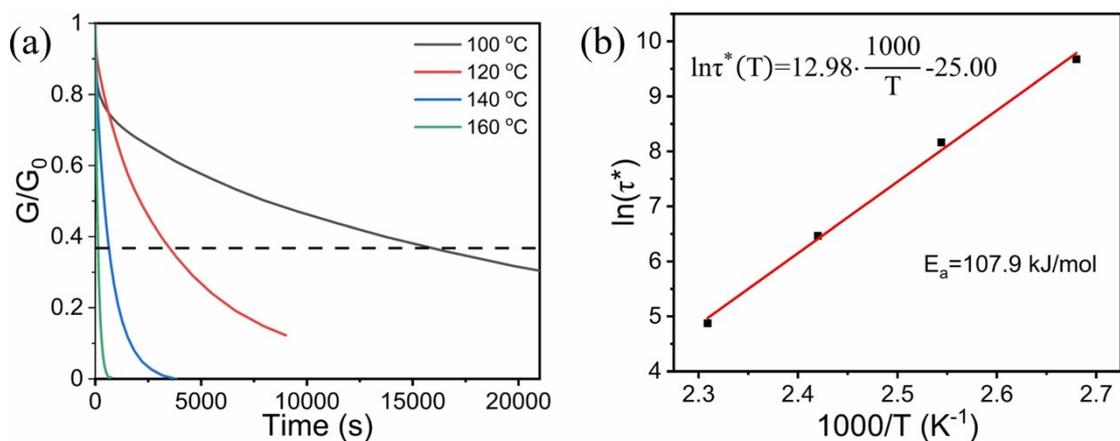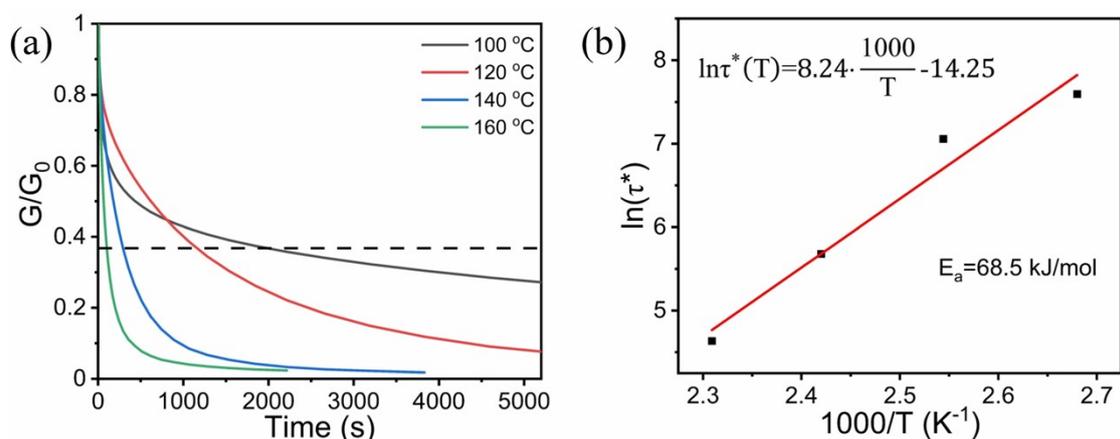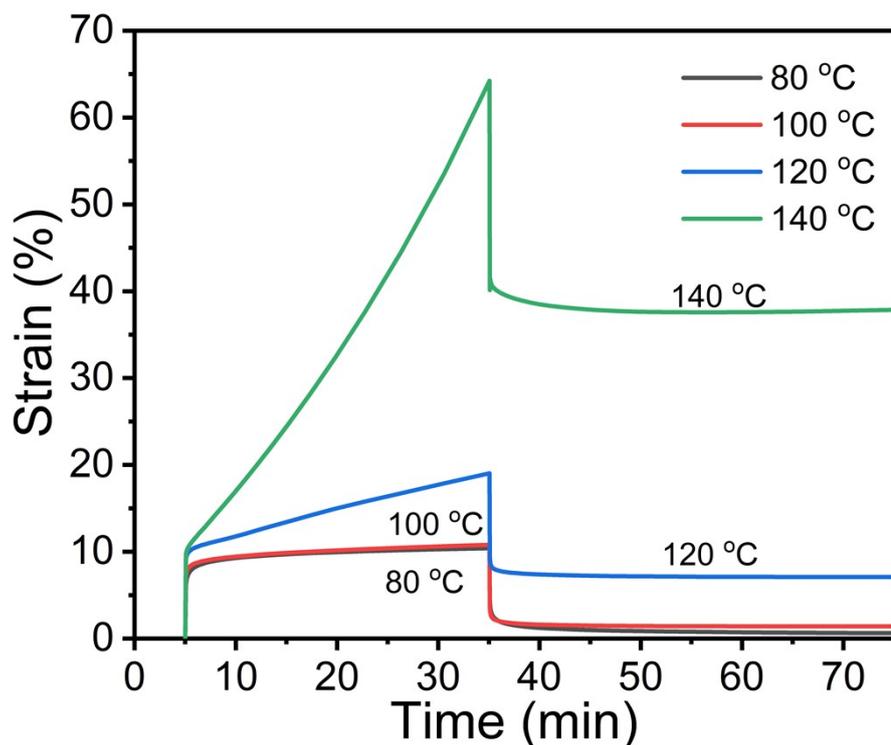
Fig. S8 Creep analysis of ACPCN35111

Table S1 Ratios of compounds

Sample	IPDI : PTMEG : HBAA : TMP
ACPCN31051	3 : 1 : 0.5 : 1
ACPCN35111	3.5 : 1 : 1 : 1
ACPCN41151	4 : 1 : 1.5 : 1
ACPCN45121	4.5 : 1 : 2 : 1

Table S2 Mechanical properties of ACPCNs

Sample	content of azine monomer (mol%)	Young's Modulus (MPa)	Stress of break (MPa)	Strain of break (%)	Toughness of (MJ·m^{-3})
ACPCN31051	9.1	10.9±1.1	22.2±2.1	511.3±7.3	38.7±3.1
ACPCN35111	15.4	113.9±3.1	44.1±3.7	512.4±29.0	101.3±11.2
ACPCN41151	20.0	312.8±39.0	53.8±2.5	489.5±15.0	138.1±8.7
ACPCN45121	23.5	502.9±69.7	51.1±3.6	505.0±44.5	156.1±19.1

Table S3 Parameters of ACPCNs

Sample	T_g (°C) DSC	DMA	GF (%)	SR (%)	ρ (g·cm^3)	E (100 °C)	ν (mol·m^{-3})	M_c (g·mol^{-1})	T_v (°C)

						(MPa)			
31051	21.6	38.9	87.1	324	1.084	1.76	189	5730	51.7
35111	27.5	55.0	86.9	370	1.095	1.43	154	7124	55.0
41151	31.8	66.3	85.8	439	1.104	2.10	226	4891	31.8
45121	47.7	71.7	79.7	483	1.113	2.89	311	3583	19.9

Table S4 Molecular weights of depolymerized and repolymerized linear polyurethanes

process	M_n	M_w	M_p	PDI
synthesized at 60 °C	26582	46927	48337	1.765
depolymerized at 150 °C	9136	12928	11410	1.415
repolymerized at 60 °C	21659	45869	40068	1.936

[1]   TRETBAR C A, NEAL J A, GUAN Z B. Direct Silyl Ether Metathesis for Vitrimers with Exceptional Thermal Stability [J]. Journal of the American Chemical Society, 2019, 141(42): 16595-16599.

[2]   XU X W, MA S Q, WANG S, et al. Dihydrazone-based dynamic covalent epoxy networks with high creep resistance, controlled degradability, and intrinsic antibacterial properties from bioresources [J]. Journal of Materials Chemistry A, 2020, 8(22): 11261-11274.

[3]   CAPELOT M, UNTERLASS M M, TOURNILHAC F, et al. Catalytic Control of the Vitrimer Glass Transition [J]. Acs Macro Letters, 2012, 1(7): 789-792.

[4]   LIU W X, ZHANG C, ZHANG H, et al. Oxime-Based and Catalyst-Free Dynamic Covalent Polyurethanes [J]. Journal of the American Chemical Society, 2017, 139(25): 8678-8684.