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

Dihydrazone-based Dynamic Covalent Epoxy Networks with High Creep Resistance, Command Degradability, and Intrinsic Antibacteria from Bioresources

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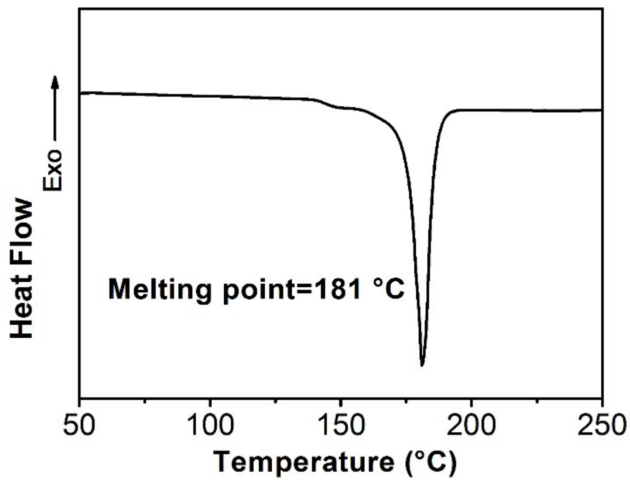

Fig. S1 Non-isothermal DSC curve of HBP.

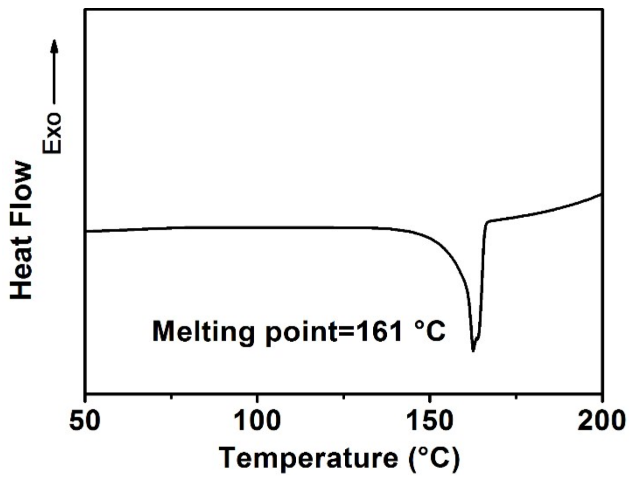

Fig. S2 Non-isothermal DSC curve of HBE.

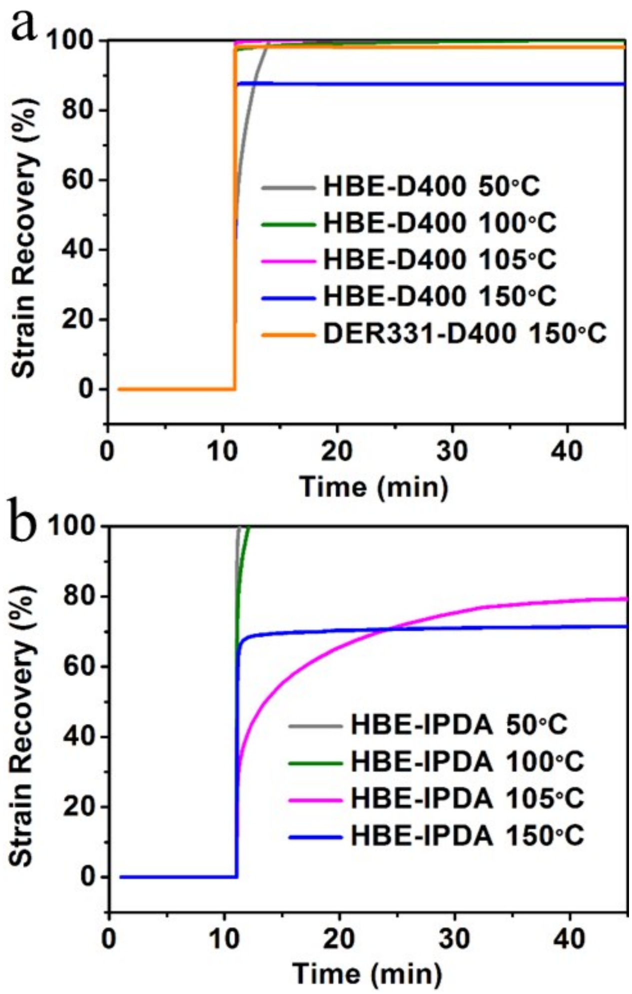

Fig. S3 Strain recovery as a function of time for a) HBE-D400 and b) HBE-IPDA during the creep tests.

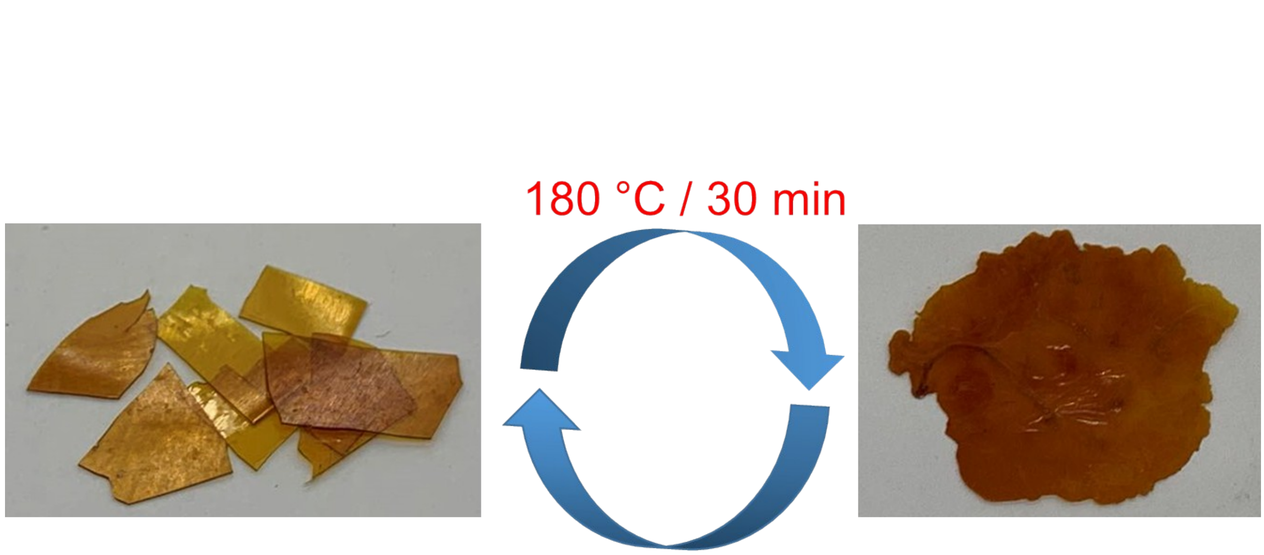

Fig. S4 Reprocess of HBE-IPDA at 180 °C for 45 min under 10 MPa pressure.

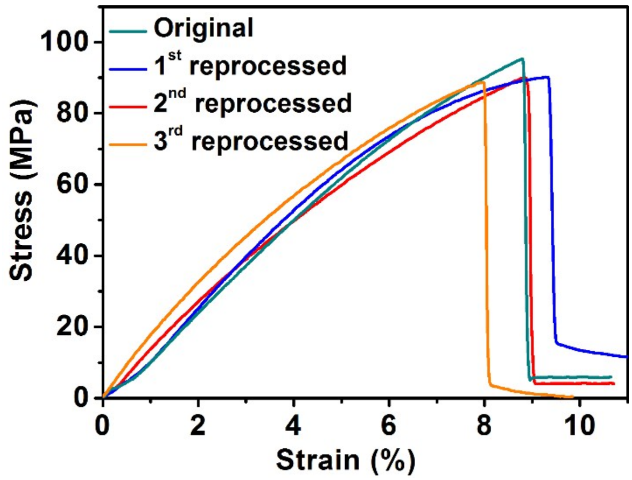

Fig. S5 Representative tensile stress−strain curves of the original and reprocessed HBE-IPDA

Table S1 Tensile properties of the original and reprocessed HBE-IPDA.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Original	1991±34	95±4	8.7±0.5
1st reprocessed	1965±26	90±3	9.3±0.3
2nd reprocessed	2044±19	89±2	8.8±0.2
3rd reprocessed	2093±17	88±2	8.0±0.2

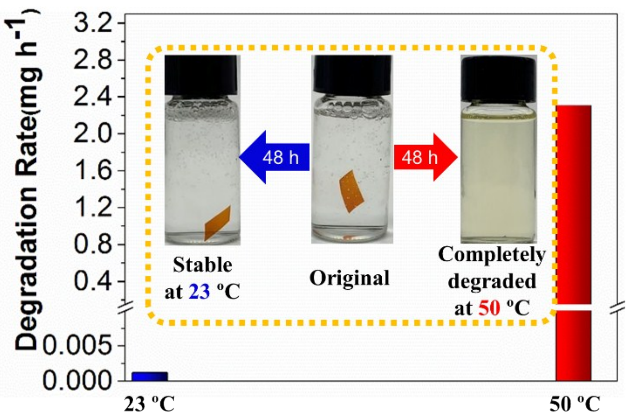

Fig. S6 Different degradation rate of HBE-IPDA in 0.1 M HCl water/acetone (2/8, v/v) solution at 23 °C and 50 °C.

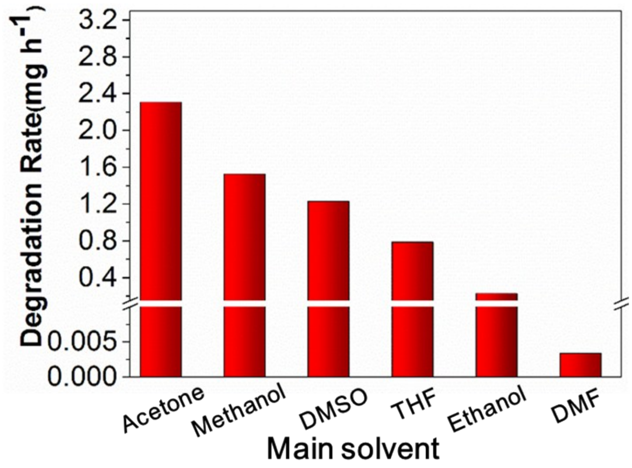

Fig. S7 Degradation rate of HBE-IPDA in 0.1 M HCl water/main solvent (2/8, v/v) solution with different main solvent at 50 °C.

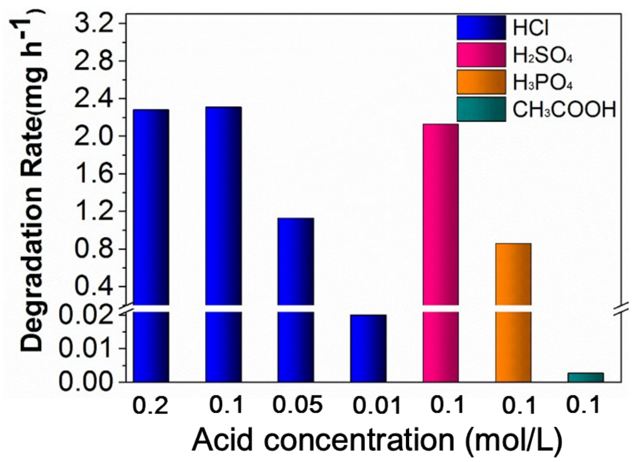

Fig. S8 Degradation rate of HBE-IPDA in different acid water/acetone (2/8, v/v) solutions at 50 °C.

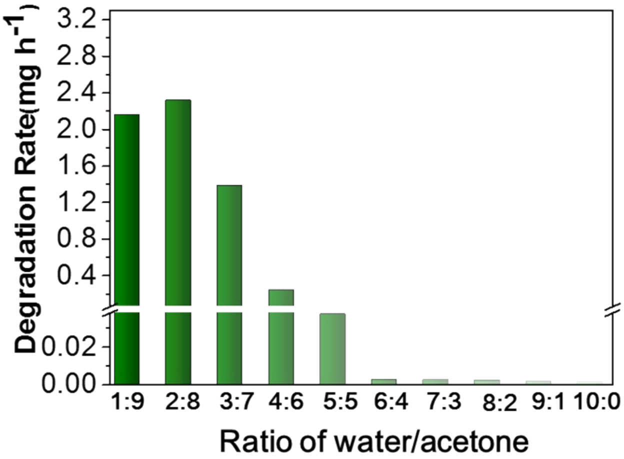

Fig. S9 Degradation rate of HBE-IPDA in 0.1 M HCl water/acetone solutions with different solvent ratios at 50 °C.

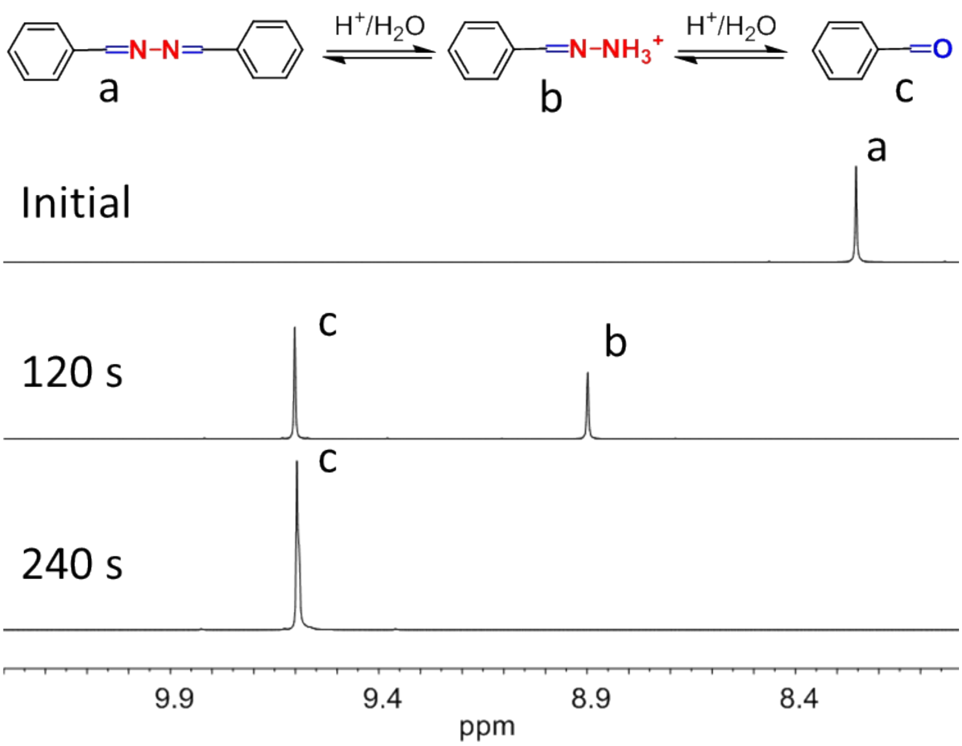

Fig. S10 The real-time ^{1}H NMR spectra of small-molecule model dihydrazone DBH after degradation at 23 °C for different times.

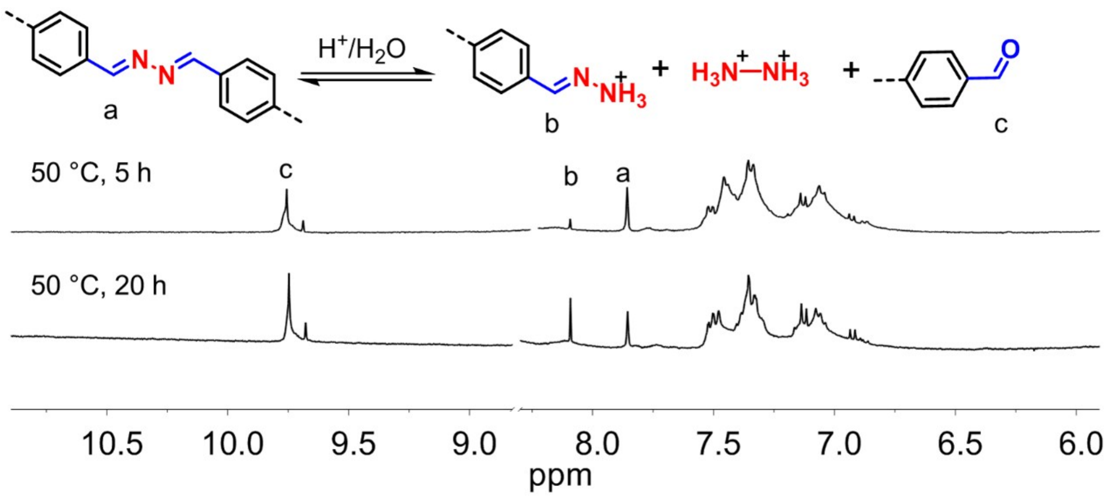

Fig. S11 The real-time 1H NMR spectra of dihydrazone CANs after degradation.

Table S2 Contact angle and swelling degree of HEB-IPDA in different solvents at 50 °C.

Main solvent	Methanol	Ethanol	THF	DMSO	DMF	Acetone									
Water/Main solvent, (v/v)	2/8	2/8	2/8	2/8	2/8	10/0	9/1	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9
Contact angle (°)	28.3	36.4	20.6	24.1	41.5	83.8	74.1	67.9	62.2	51.7	42.9	39.7	34.6	28.1	23.8
Swelling degree (%)	25	9	18	21	5	1	1	5	7	9	13	17	23	27 (1*)	31

*: Swelling test at 23 °C

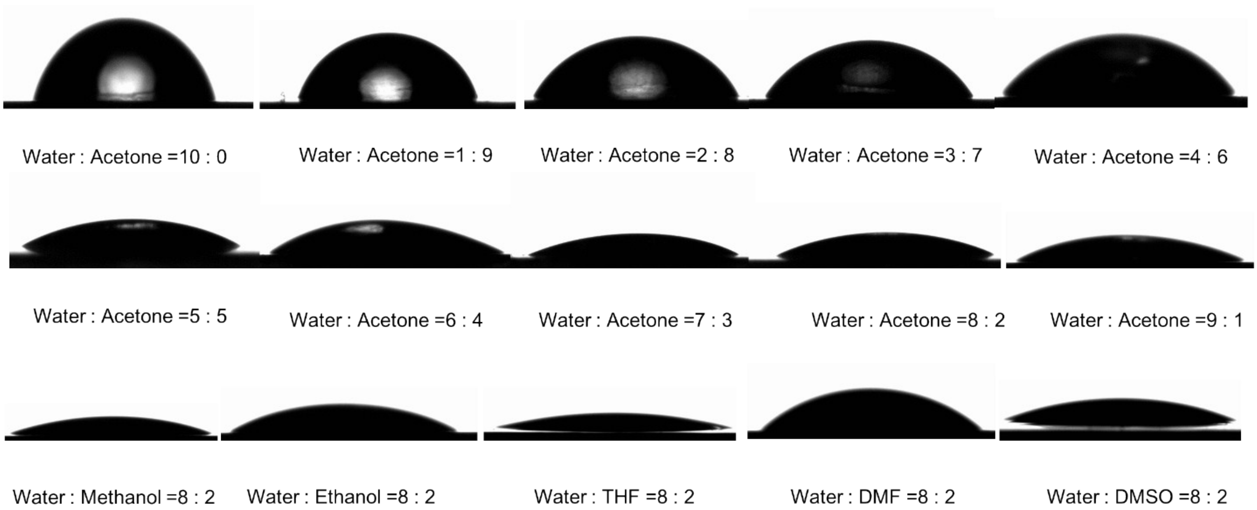

Fig. S12 Digital photographs of static contact angle of HBE-D400.

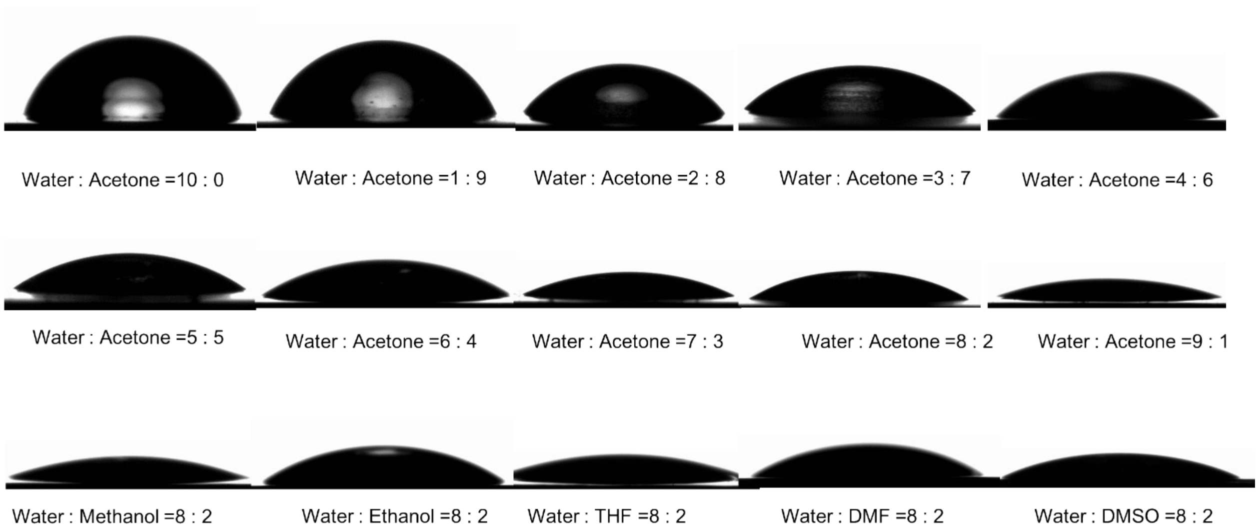

Fig. S13 Digital photographs of static contact angle of HBE-IPDA.

Calculation of topology-freezing temperatures (T_vs) and activation energies (E_as).

Topology-freezing temperatures (T_v) and activation energies (E_a) were determined using the methodology reported in literature[1, 2]. The measured values of characteristic relaxation times (τ*s) were plotted versus 1000/T. The plots were fit to the Arrhenius law in equation (1)

$$\tau^* (T) = \tau_0{}^* e^{E_a/RT} \quad (1)$$

(R : universal gas constant; 8.314 J K^{-1} mol^{-1})

Equation (1) can be transformed to equation (2):

$$ln\ \tau^* (T) = ln\ \tau_0{}^* + E_a/RT \quad (2)$$

For HBE-D400:

$$ln\ \tau^* (T) = 11.458 \times \frac{1000}{T} - 17.154 \quad (3)$$

E_a/R =11.458, E_a = 95.26 kJ mol^{-1}

For HBE-IPDA:

$$ln\ \tau^* (T) = 11.208 \times \frac{1000}{T} - 17.145 \quad (4)$$

E_a/R = 11.208, E_a = 93.18 kJ mol^{-1}

T_v is defined to be the temperature at which the material reaches a viscosity of 10^{12} Pa. The relation of the viscosity η and the τ* is known as the Maxwell relation equation (5)

$$\eta = G \times \tau^* = (E'/2\ (1 + v)) \times \tau^* \quad (5)$$

(G : shear modulus, E' : storage modulus, v : Poisson's ratio)

Using the Poisson's ratio (v) of epoxy resin (0.38),

$$\eta = 0.284 \times E' \times \tau^* \quad (6)$$

The storage modulus of HBE-D400 from 170 °C to 185 °C is 9.3 MPa, and that of HBE-IPDA in the same temperature range is 13.1 MPa. Because η is 10^{12} Pa at T_v, τ*s at T_v of HBE-D400 and HBE-IPDA are calculated to be 3.9× 10^5 s and 2.7× 10^5 s, respectively. Using these values and equation (3) and (4), T_v was computed to be 109 °C for HBE-D400 and 105 °C for HBE-IPDA.

References

1 M. Capelot, M. M. Unterlass, F. Tournilhac, L. Leibler, *ACS Macro Lett.,* 2012, **1**, 789-792.

2 C. A. Tretbar, J. A. Neal, Z. Guan, *J. Am. Chem. Soc.,* 2019, **141**, 16595-16599.