Supporting Information for

Development of Tough and Stiff Elastomers by Leveraging Hydrophilic–Hydrophobic Supramolecular Segment Interaction

Jihua Yang[a,b], Wei Zhang[a,b], Rui Pan[a,b], Yizhi Zhuo[*a], Hua Cheng[c,e], Awang Zhang[f], Mengru Liu[a,b], Zeqing Wang[e], Yi Gong[*a], Rui Hu[a], Jianjun Ding[a,d], Lin Chen[a], Xian Zhang[a], Xingyou Tian[*a]

Corresponding to *E-mail: yz.zhuo@foxmail.com, yigong@rntek.cas.cn (Y. Gong),xytian@issp.ac.cn (X. Tian)

Supporting Information Text

Synthesis of $PDdi_{2000}$ and $PDbi_{2000}$

$PDdi_{2000}$: Chain extension reaction was used to synthesize $PDdi_{2000}$, as shown in Figure S1, Supporting Information. The specific process is as follows: Isophorone diisocyanate (IDI, 4.2237 g, 19 mmol, Sigma-Aldrich) was dissolved in tetrahydrofuran (THF, 15 mL, Sigma-Aldrich) under vigorous stirring. Then the polyetheramine (PEA, 19.000 g, 9.5 mmol, molecular weight: 2000 Dalton, Sigma-Aldrich) was dissolved in tetrahydrofuran (THF, 75 mL, Sigma-Aldrich) and dropwise added into the above solution. After stirring for 2 h, 1,8-diaminooctane (1.3705 g, 9.5 mmol, chain extender, Sigma-Aldrich) which was dissolved in THF (15 mL) was added into the mixture under vigorous stirring. After stirring for another 24 h, the viscous mixture was stored for further fabrication or testing.
$PDbi_{2000}$: Its synthesis method is basically consistent with $PDdi_{2000}$. The difference is that after stirring for 2 h, 1,2-bis(2-aminoethoxy)ethane (1.4080 g, 9.5 mmol, chain extender, Sigma-Aldrich) which was dissolved in THF (15 mL) was added into the mixture under vigorous stirring.

Fabrication of $PDdi_{2000}$ and $PDbi_{2000}$ films for testing

75 mL of the above solution was poured into a cuboid Teflon pool mould with a dimension of 12 × 12 × 1.2 cm^3, covered by lid with holes and allowed to dry under a fume hood for 3 days. Then, the obtained elastomer film was carefully peeled off from the mould.

Mechanical testing

Tensile tests were carried out on a mechanical testing system at 25 °C (Instron 5944 with a 2 kN load cell). Dumbbell shaped sample (15.0×2.0×1.0 mm) were prepared, and the stretching rate was set at 50 mm min^{-1}. The fracture energy test was measured through the tensile test using a single-edge notch sample at the tensile speed of 45 mm min^{-1}. Both the notched and unnotched samples (gauge length of 30.0 mm, thickness of 1.0 mm, and width of 10.0 mm) were measured. The specific shape is shown in Fig. 4d. The fracture energy

(Gc) of $PDdi_{2000}$ and $PDbi_{2000}$ was characterized by the following equation:

$$G_c = \frac{6Wc}{\sqrt{\lambda_c}} \quad (1)$$

Where c represents the length of the notch (2 mm), λ_c is the value of the elongation at break of the notched sample, W is the strain energy which is calculated by integrating the stress-strain curve of the unnotched sample until elongation at break. Young's modulus (E) of $PDdi_{2000}$ and $PDbi_{2000}$ was obtained from fitting slope of initial stress-strain curves of uniaxial tensile test.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrum was tested by a FTIR spectrometer (Thermo Nicolet Nexus) equipped with a temperature controller. To investigate the movement of infrared spectra during the heating process, the spectra after 9 ℃ from 35 ℃ to 150 ℃ were recorded.

^{1}H nuclear magnetic resonance (NMR) spectroscopy

^{1}H-NMR spectrum was recorded on a Bruker AVANCE III (400MHz) spectrometer with chloroform ($CDCl_3$, Sigma-Aldrich) as the solvent.

Thermogravimetric analysis (TGA)

TGA was measured by using a Netzsch instrument (TG 209F1 Libra). The specimen was placed in the crucible and heated from 35 ºC to 700 ºC with a heating rate of 15 ºC/min under nitrogen atmosphere.

X-ray photoelectron spectroscopy (XPS)

XPS was measured in the Kratos Ultra DLD with 12kV and 12mA by a monochromatic Al source. The pressure of chamber was 5×10^{-9} mbar. The CasaXPS software was used to analyze the data. All binding energies were referenced to the C 1s peak at 285 eV of the

surface adventitious carbon. Then a five-point quadratic Savitzky-Golay algorithm was used to process the data.

Differential scanning calorimetry (DSC)

The sample was measured using a DISCOVER DSC 250 (TA Instruments, America) apparatus. All specimens were heated from -100 ℃ to 150 ℃ at a heating rate of 10 ℃ min^{-1} under liquid nitrogen.

Atomic force microscopy (AFM)

AFM was measured in the Veeco Metrology machine (diMultimode V) with PeakForce Quantitative NanoMechanics mode. ScanAsyst-Air probe (Bruker) was employed for measurements.

Dynamic mechanical analyses (DMA)

DMA were performed on the Dynamic Mechanical Analyzer Q800 (TA Instrument, Waters Ltd.) under the tension mode in the temperature range from -100 to 150 °C at a heating rate of 5 °C min^{-1}.

X-ray diffraction (XRD)

XRD was conducted on a D8 DISCOVER X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm).

Tandem gel permeation chromatography (GPC)

GPC was performed in THF with a flow rate of 1.0 mL min^{-1} and 0.1 M LiBr at 40 °C. Separations were got by series-connected size exclusion columns (103 Å, 400 Å, and 5 μm, 300 × 7.8 mm, 104 Å phenol gel columns, Torrance, Phenomenex, CA) on a system endowed with an isocratic pump.

Small angle X-ray Scattering (SAXS)

Two-dimensional (2D) SAXS patterns were achieved by a Bruker NANOSTAR instrument. Each 2D SAXS pattern was got by subjecting the elastomer to the X-ray source for a duration of 10 minutes. The sample to detector distance was 1060 mm and the wavelength of the X-ray radiation was 0.154 nm. The 1D SAXS curves were obtained by the DIFFRAC-SAXS software. The periodicity (L) was figured out by Bragg's Law:

$$L = \frac{2\pi}{q_{max}} \tag{2}$$

where q_{max} represents the peak location of the 1D SAXS curve.

Transmittance

Transmittance of specimen was calculated by a spectrophotometer (Cary 14 UV/Vis/NIR) in the wavelength range of 400 to 800 nm.

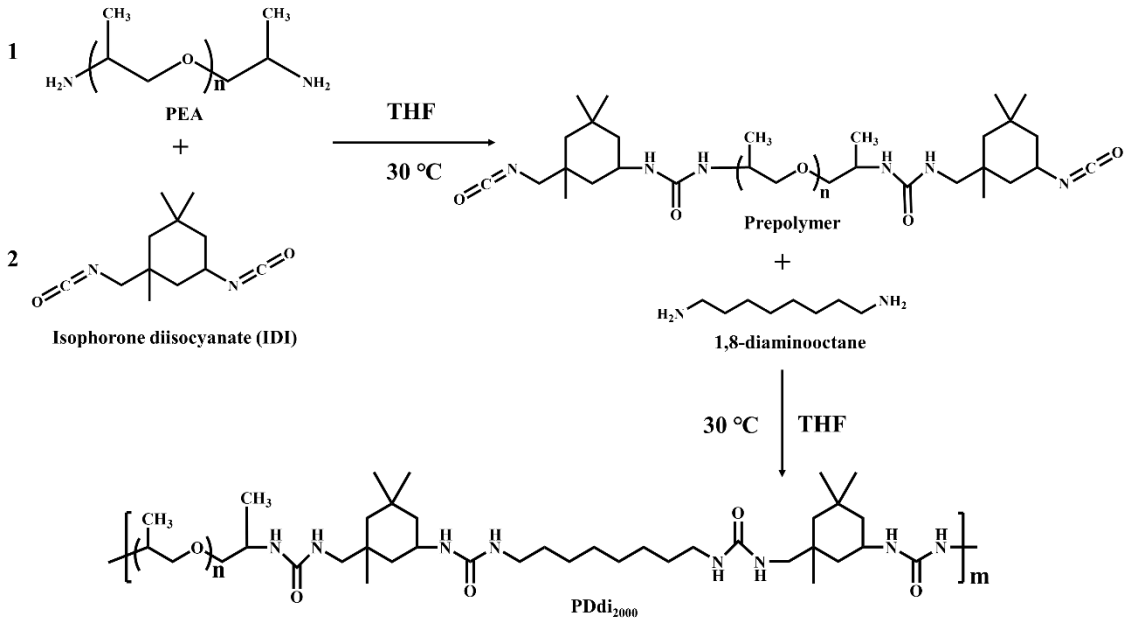


Fig. S1 $PDdi_{2000}$ was synthesized by the chain extension reaction.

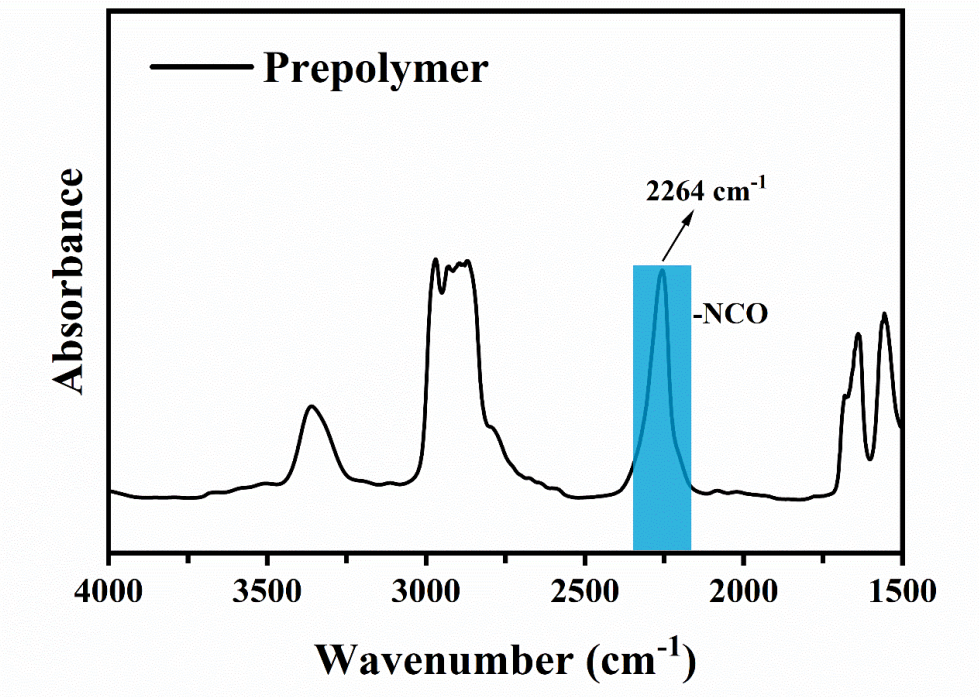


Fig. S2 FTIR spectra of the NCO-terminated prepolymer.

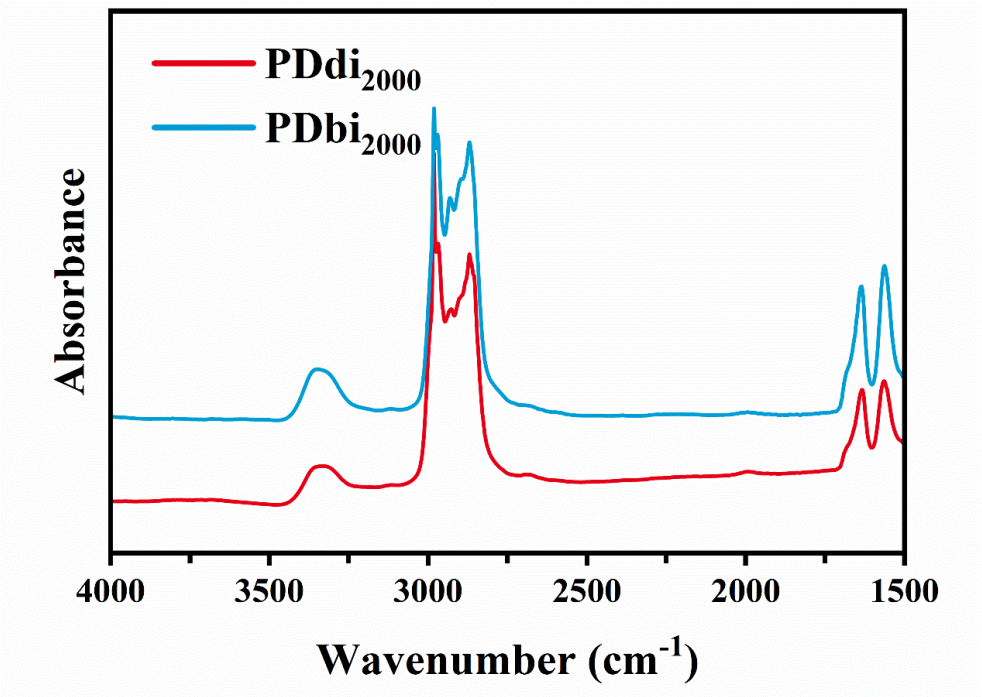


Fig. S3 FTIR spectra of $PDdi_{2000}$ and $PDbi_{2000}$ in the wavenumber range of 4000-1500 cm^{-1}.

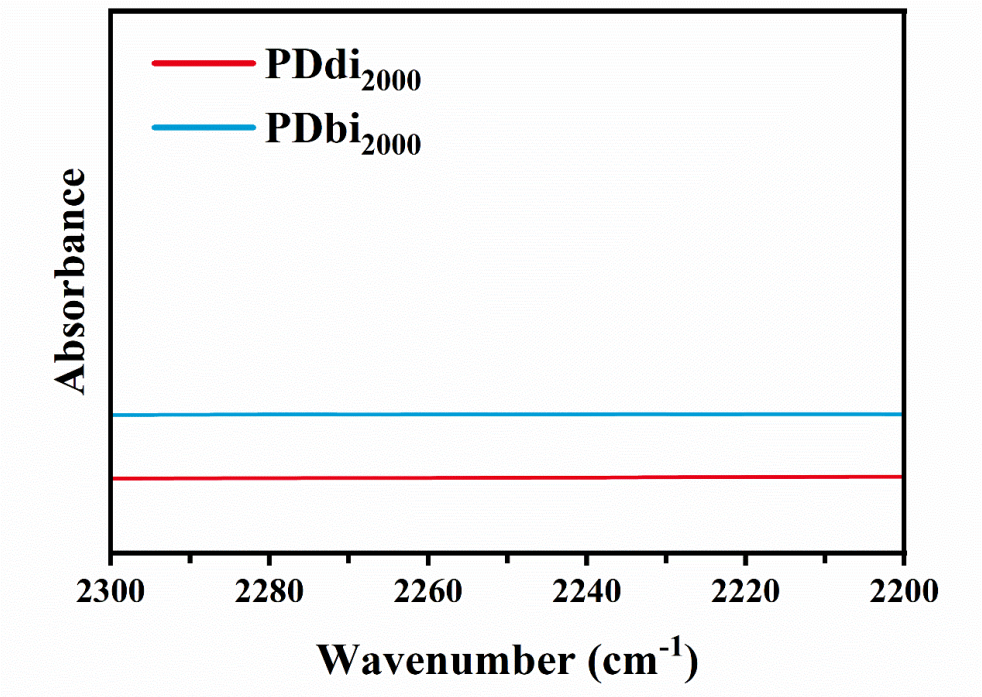


Fig. S4 FTIR spectra of $PDdi_{2000}$ and $PDbi_{2000}$ in the wavenumber range of 2300-2200 cm^{-1}.

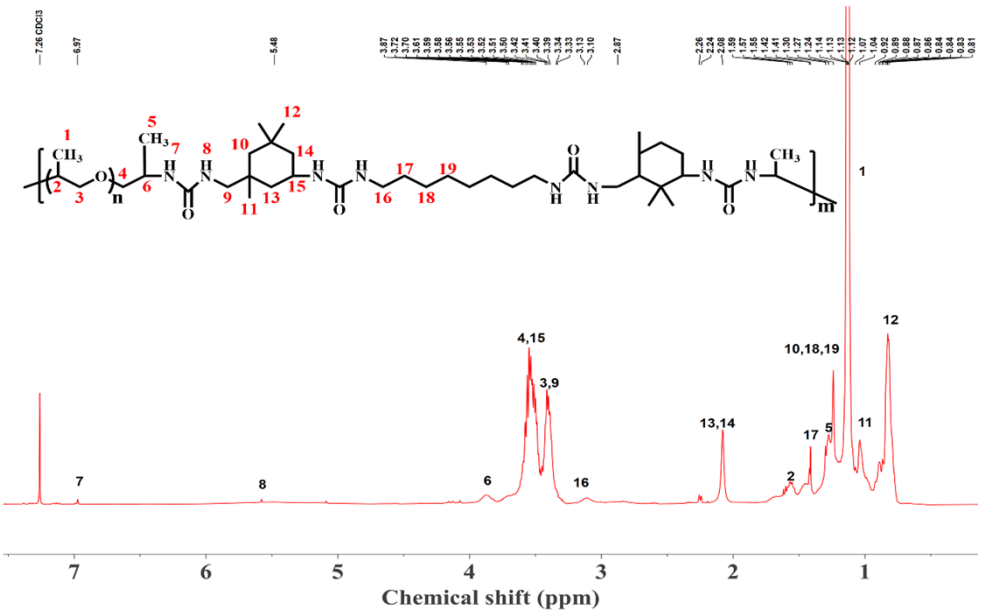


Fig. S5 ^{1}H NMR spectra of PDdi$_{2000}$.

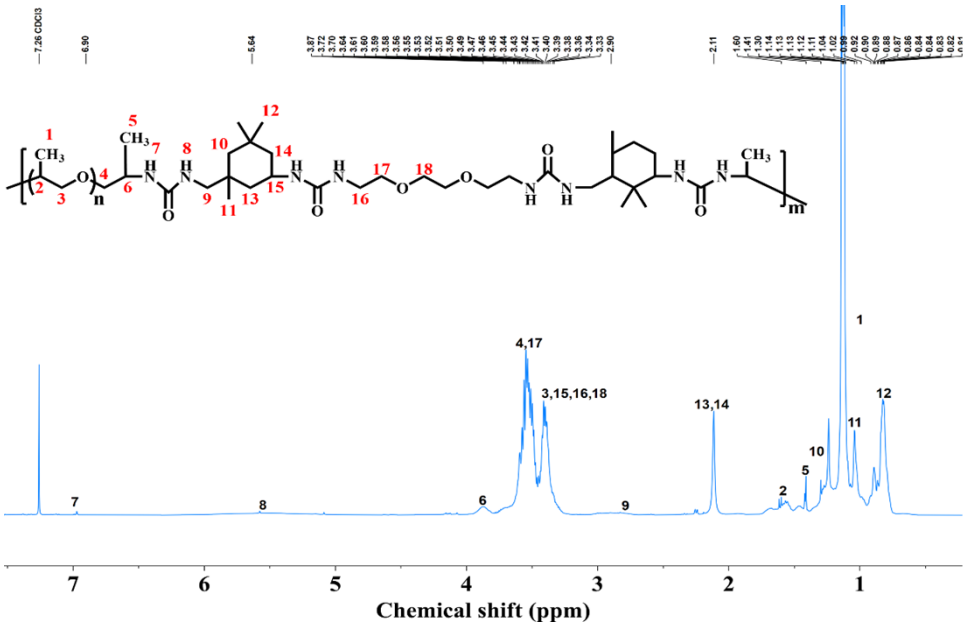


Fig. S6 ^{1}H NMR spectra of $PDbi_{2000}$.

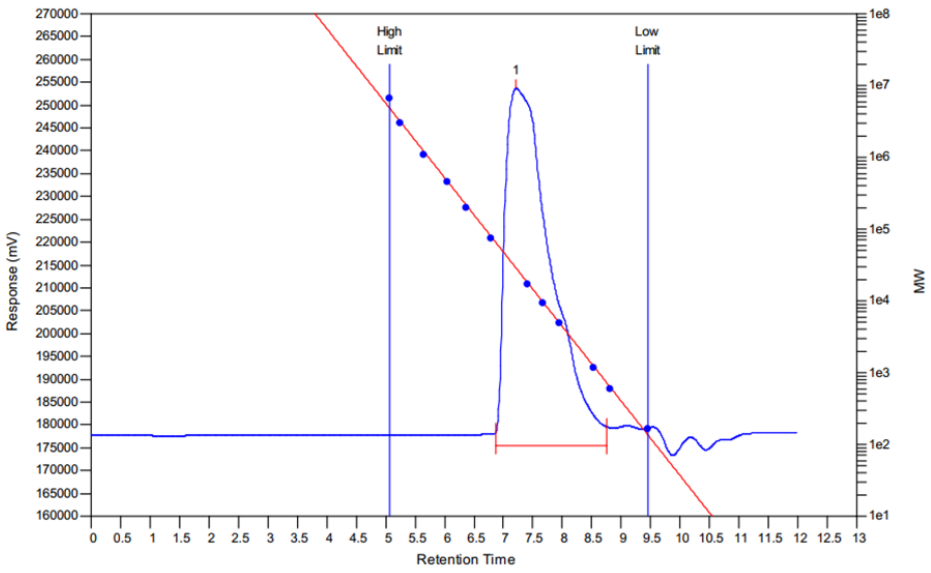


Fig. S7 GPC traces recorded for $PDdi_{2000}$.

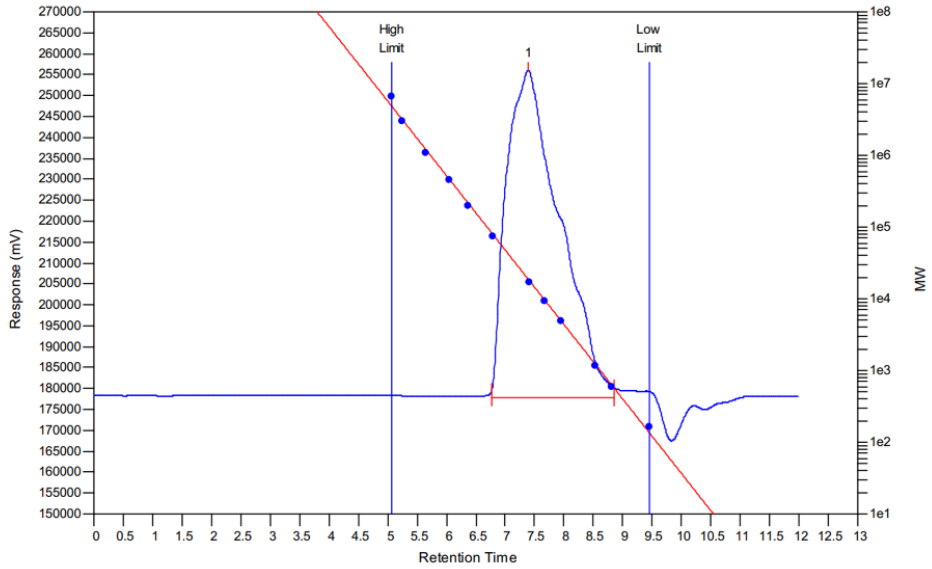


Fig. S8 GPC traces recorded for $PDbi_{2000}$.

Sample	Mp	Mn	Mw	PD
PDdi$_{2000}$	28660	8103	18897	2.332
PDbi$_{2000}$	18962	6920	18879	2.728

Table S1. Analysis of GPC test results.

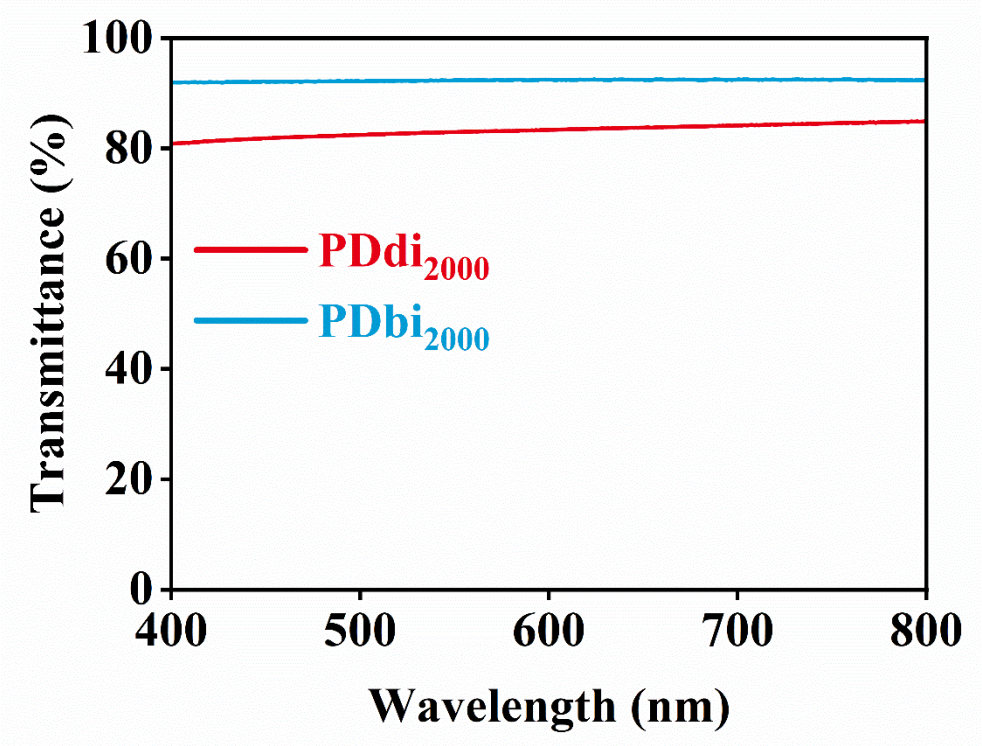


Fig. S9 UV–vis transmission spectra of $PDdi_{2000}$ and $PDbi_{2000}$.

Group	Bonding situation	Wavenumber (cm^{-1}) **$PDdi_{2000}$** **$PDbi_{2000}$**
υ (C=O) Urea carbonyl	**Free**	I (1678) I (1681)
	H-bonded (Disordered)	II (1651) II (1651)
	H-bonded (Ordered)	III (1633) III (1633)
Degree of H-Bonded (Ordered)		**55.09** **38.77**
Degree of H-Bonded (Disordered)		**28.79** **46.08**
Degree of Free		**16.43** **15.15**

Table S2. Summary of the assignment of the deconvoluted subpeaks in the FTIR C=O absorption bands for $PDdi_{2000}$ and $PDbi_{2000}$.

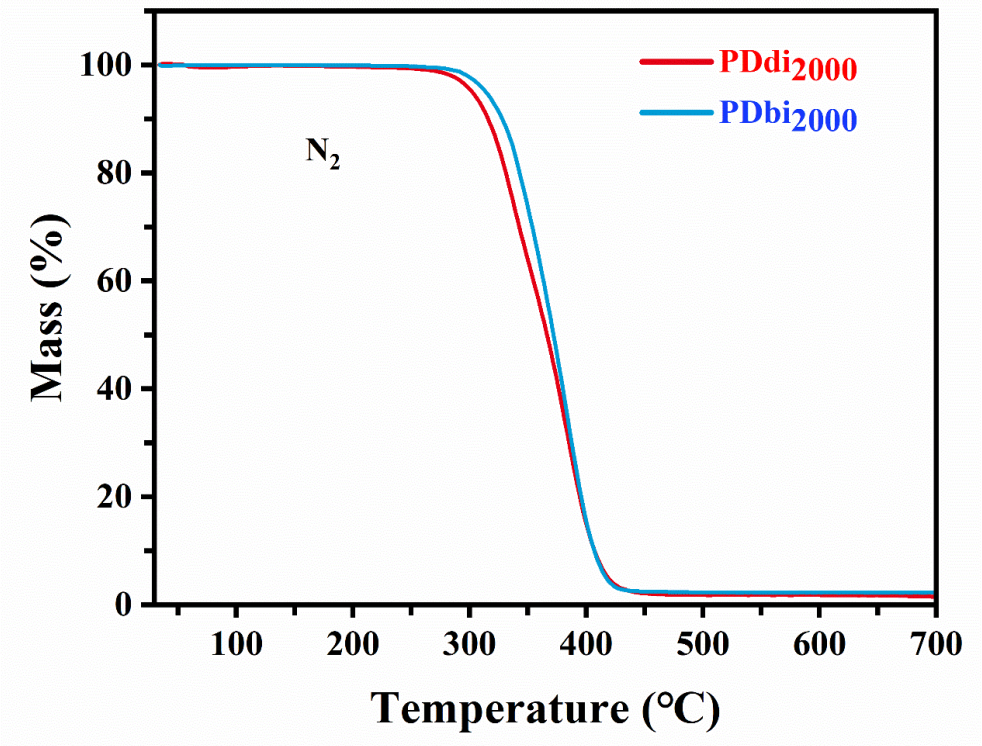


Fig. S10 TGA curves of $PDdi_{2000}$ and $PDbi_{2000}$. There is no clear degradation below 300 ºC.

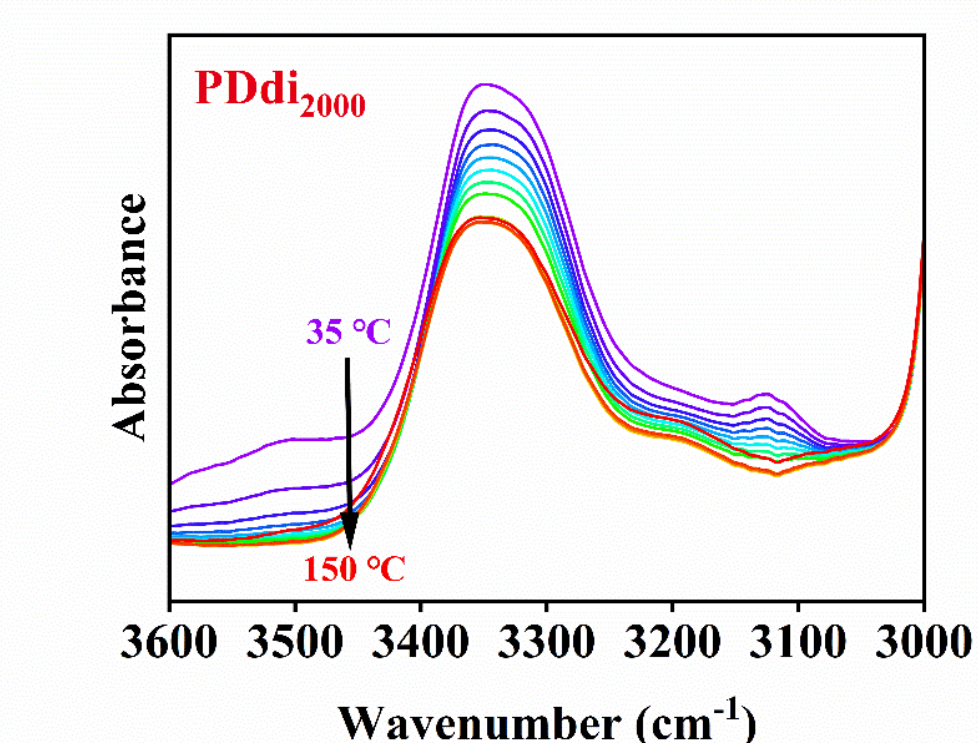


Fig. S11 FTIR spectra of $PDdi_{2000}$ at an increasing temperature from 35 ºC to 150 ºC in the range of 3600 to 3000 cm^{-1}.

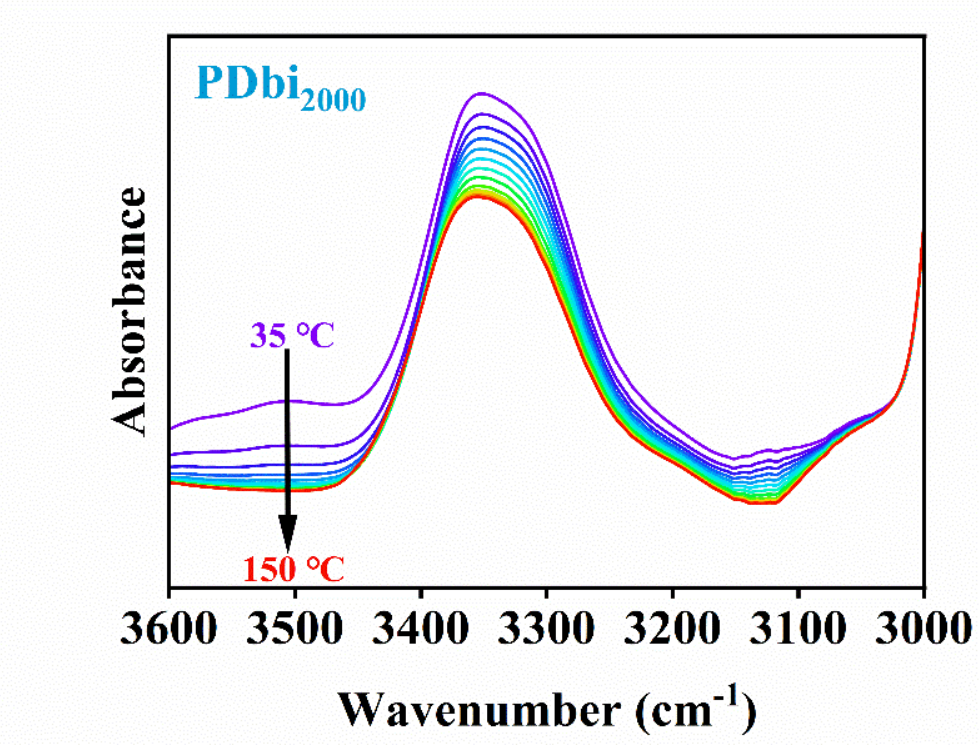
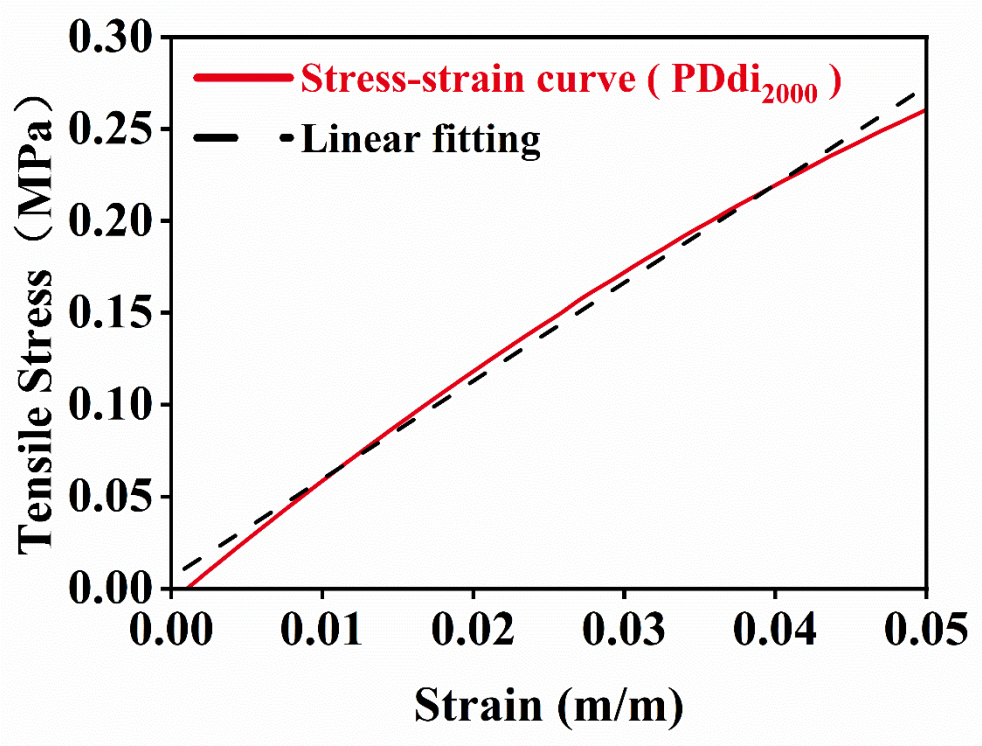
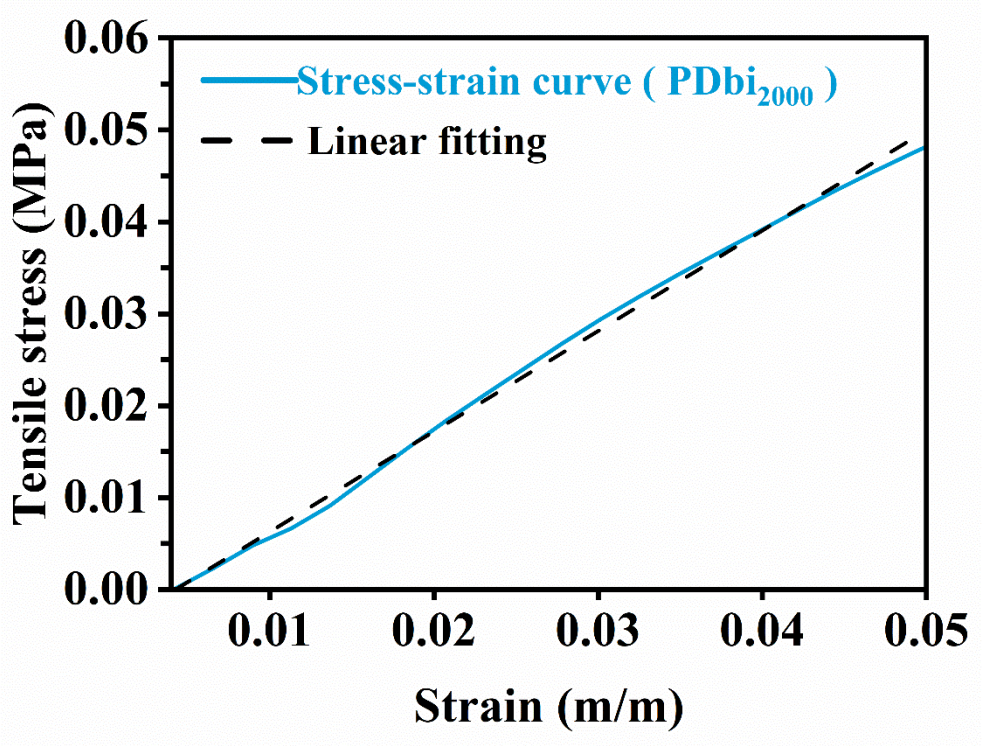


Fig. S12 FTIR spectra of $PDbi_{2000}$ at an increasing temperature from 35 ºC to 150 ºC in the range of 3600 to 3000 cm^{-1}.





Figs. S13 The initial parts of stress-strain curves of the uniaxial tensile test of $PDdi_{2000}$ and $PDbi_{2000}$. The curves are linearly fitted to obtain the slopes corresponding to Young's modulus. The obtained values are reported in Fig.5f

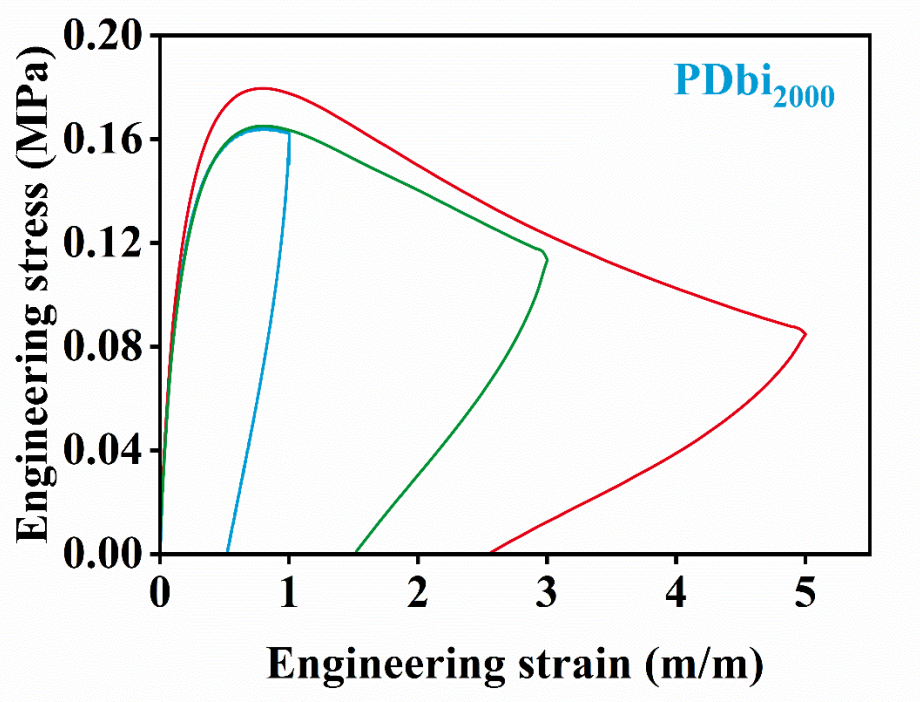


Fig. S14 $PDbi_{2000}$ is subjected to cyclic loading/unloading tests with different maximum tensile strains.

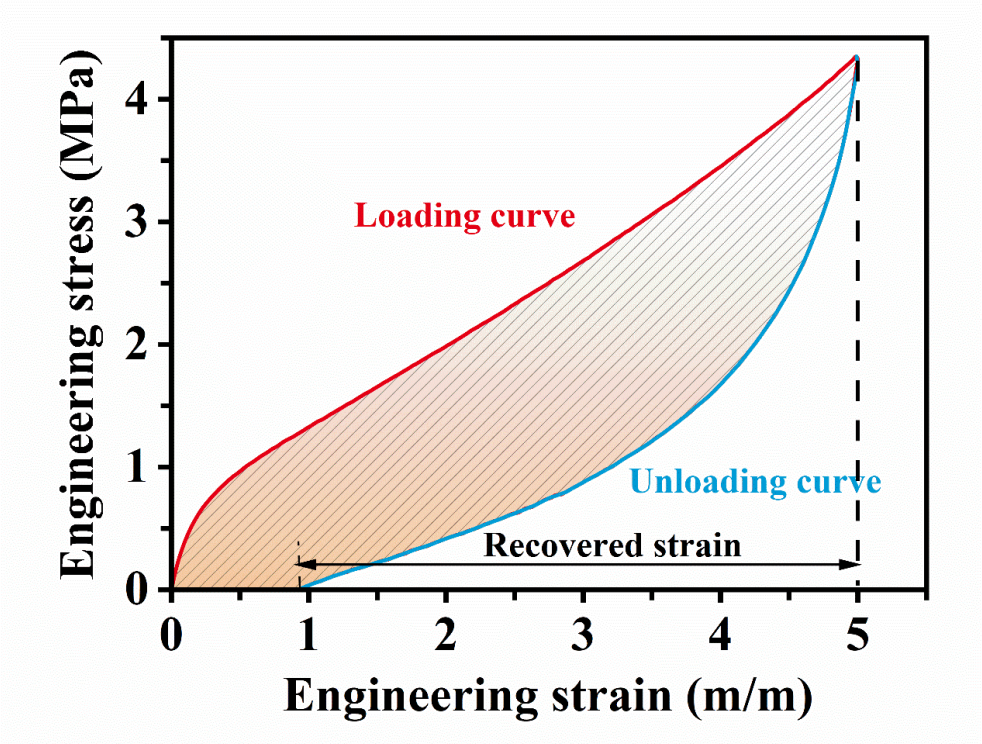
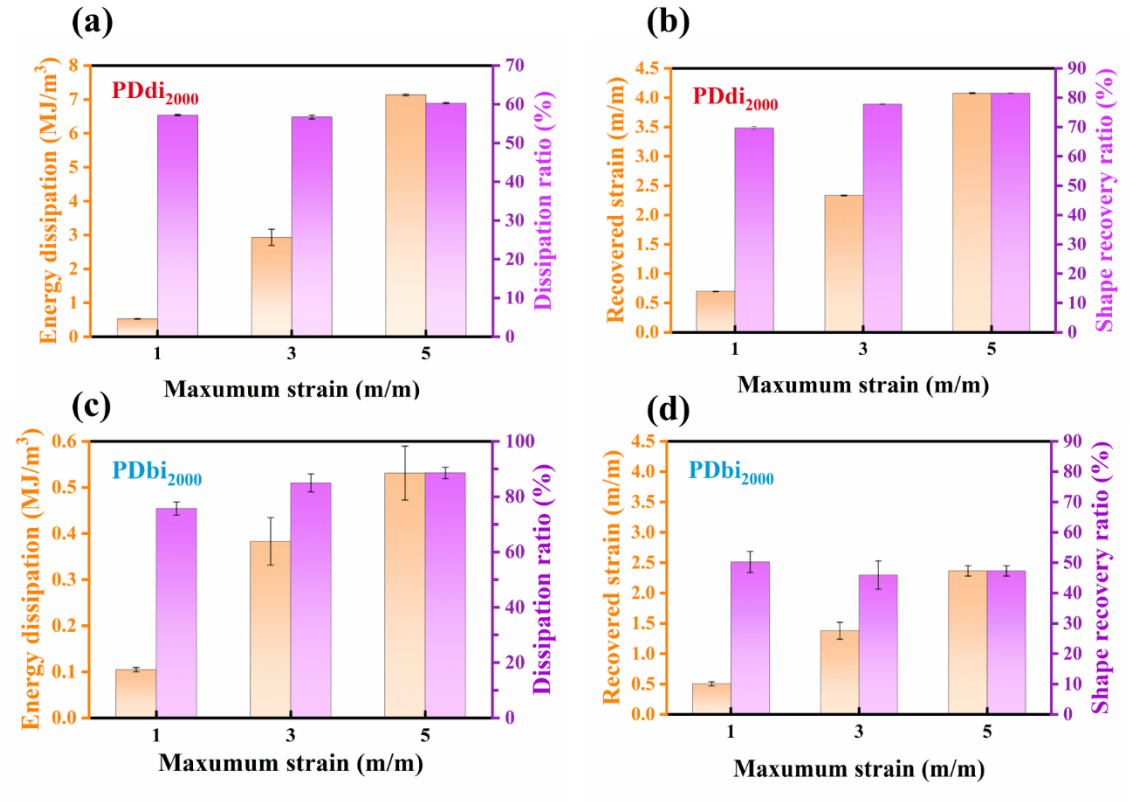


Fig. S15 Typical cyclic loading/unloading curves of PDdi2000 and PDbi2000. The red line is the loading curve, while blue line is the unloading curve. The orange area between the loading and unloading curves denotes the energy dissipation. Recovered strain is denoted by the black arrow.



Figs. S16 (a, c) Energy dissipations and dissipation ratios at different maximum strains. The dissipation ratio is the ratio between energy dissipation and loading energy (i.e., the area under the loading curve). (b, d) Recovered strains and shape recovery ratios at different maximum strains. The shape recovery ratio is the ratio between recovered strain and maximum strain.

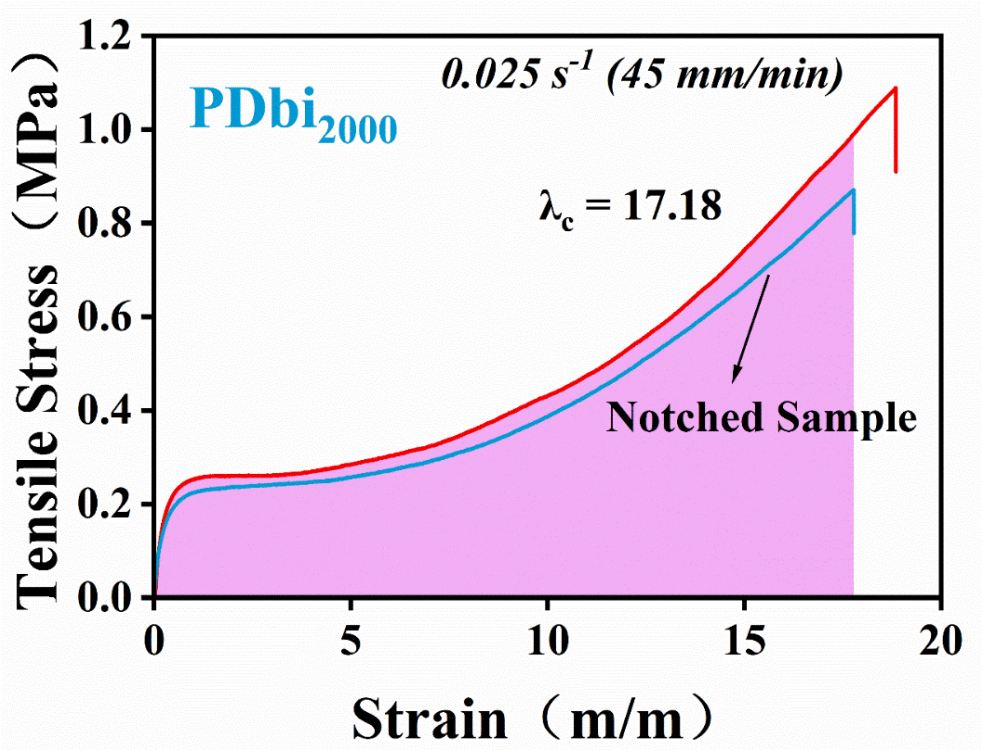


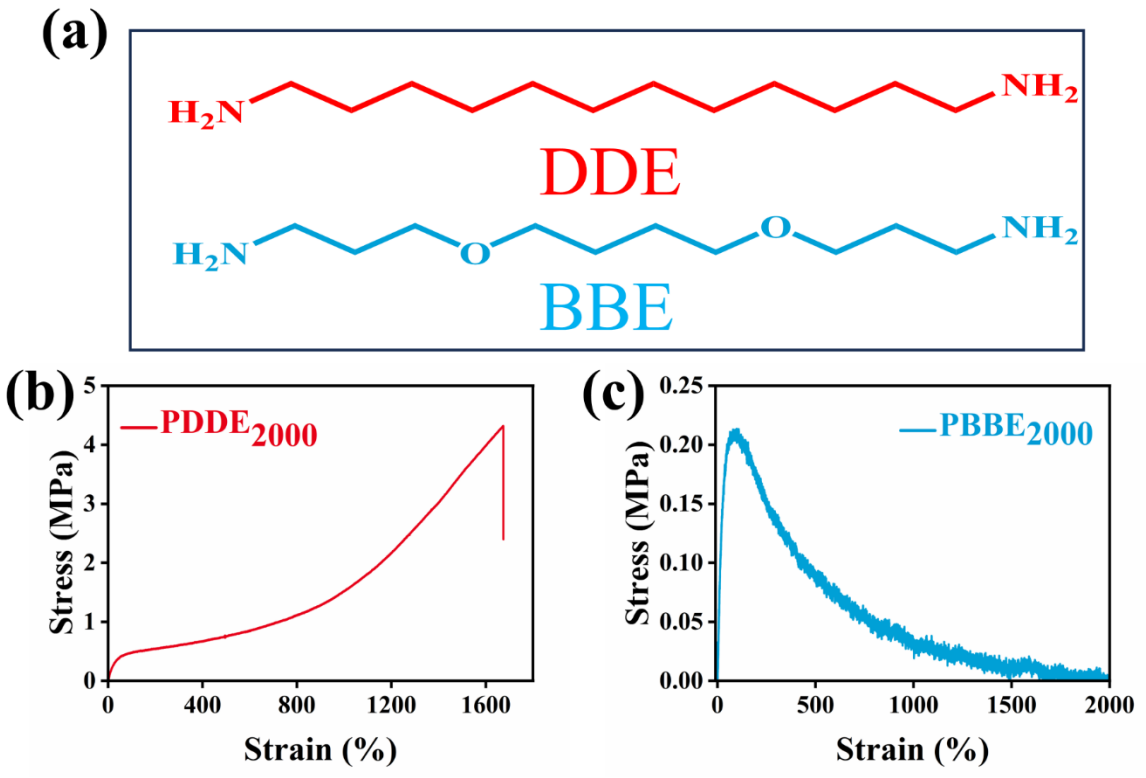
Fig. S17 Notched tensile test curves of $PDbi_{2000}$.

	45 mm min^{-1}	100 mm min^{-1}	200 mm min^{-1}	300 mm min^{-1}
Tensile strength (MPa)	15.70	24.95	32.72	28.85
Strain (m/m)	14.77	12.46	10.15	9.22

Table S3. The tensile stress and strain corresponding to $PDdi_{2000}$ under different stretching rates.

	45 mm min^{-1}	100 mm min^{-1}	200 mm min^{-1}	300 mm min^{-1}
Tensile strength (MPa)	0.18	0.73	0.65	0.69
Strain (m/m)	The material did not fracture			

Table S4. The tensile stress and strain corresponding to $PDbi_{2000}$ under different stretching rates.



Figs. S18 Verification of toughening mechanism. (a) Hydrophobic chain extender DDE and hydrophilic chain extender BBE. (b, c) Pure shear test of $PDDE_{2000}$ and $PBBE_{2000}$.