

Electronic Supplementary Information (ESI) for

Tunable shape memory properties of highly stretchable poly(ester urea)
random copolymers based on α -amino acids

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1. Characterization details

Nuclear magnetic resonance (NMR) spectra of the poly(ester urea) (PEU) random copolymers were obtained using DMSO- d_6 as the solvent and recorded at either 600 MHz (^1H NMR), or 126 MHz (^{13}C NMR) as noted. In all spectra, chemical shifts are given in δ relative to the solvent. The abbreviations were used to explain the multiplicities: s = singlet, d = doublet, m = multiplet. Fourier transform-infrared spectroscopy (FT-IR) spectra of the PEUs were recorded on spectrometer from 500 to 4000 cm^{-1} . Resolution was 4 cm^{-1} and scan numbers were 64. Each sample was prepared either by powder or by thin film. Weight-average molecular mass (M_w) and molecular weight distribution (D_M) of the PEUs were determined by gel permeation chromatograph (GPC, TOSOH HLC-8320) with refractive index (RI) detector and polystyrene standards. The characterizations were performed with a flow rate of 1 mL/min using HPLC grade LiBr-containing (0.01 M) DMF as the eluent at 50 °C.

For further characterizations, PEU thin films were prepared using a vacuum compression machine at 100 °C. Decomposition temperature (T_d) of the PEUs was determined by thermogravimetric analysis (TGA, Q500 TA), with a range of 25 °C to 600 °C and a heating rate of 20 °C/min. The tests were implemented under nitrogen and the T_d was reported as 10% decomposition temperature. Glass transition temperature (T_g) of the PEUs was determined by differential scanning calorimetry (DSC, Q200 TA), with a temperature range of -50 °C to 150 °C and a heating/cooling rate of 20 °C/min. The T_g was reported as the temperature corresponding to the midpoint of the “step” in the second heating cycle. The T_g was also determined by dynamic mechanical analysis (DMA, Q800 TA) 1 Hz-frequency temperature sweep experiments, with a temperature range of -50 °C to 120 °C and a heating/cooling rate of 3 °C /min. The specimens were in a dimension of 25 × 5 × 0.5 mm. The T_g was reported as the temperature corresponding to the peak on the plot of loss modulus (E'') versus temperature.

Tensile testing of the PEUs was implemented at 35 ± 1 °C based on an Instron 5543 Load Frame Instrument, which was equipped with a heating chamber and associated with Merlin Software. The specimens were in a dimension according to the Type V specimen in ASTM standard D638-14 except that the thickness was 0.5 mm. All the tests were conducted in a crosshead rate of 100 mm/min. The l_0 was 10 mm, measured with a caliper prior to the tests. For each material, three individual tests were implemented. Young's modulus (E), yield point, stress at break (σ_{break}) and strain at break (ϵ_{break}) were determined from the plots of stress versus strain. The E was reported based on the slope of stress versus strain in the linear region. For each material, the reported value was the average value of three individual test results.

2. Synthesis details

2.1 Synthesis of diamine monomers. α -Amino acid (332.90 mmol, 2.30 mol. equiv.), 1,8-octanediol (144.74 mmol, 1.00 mol. equiv.) and *p*-toluene sulfonic acid monohydrate (347.38 mmol, 2.40 mol. equiv.) were added to a round bottom flask. The mixture was dissolved in toluene (600 mL) under magnetic stir, and then the flask was fit with a Dean-Stark trap and condenser. The reaction solution was heated to reflux for 12 h. Afterwards, the reaction mixture was cooled to room temperature and the toluene was rotary-evaporated. The raw product was recrystallized from deionized water four times and dried in a vacuum oven, to yield a white powder. The chemical structure of the product was characterized by $^1\text{H-NMR}$ and FT-IR spectroscopy.

$^1\text{H NMR}$ (600 MHz, $\text{DMSO-}d_6$, δ): 8.26 (s, 6H), 7.49 (d, 4H), 7.12 (d, 4H), 4.14 (m, 6H), 3.30 (s, H_2O), 2.50 (m, DMSO), 2.29 (s, 6H), 1.60 (m, 4H), 1.28-1.39 (m, 14H). FT-IR (cm^{-1}): 1736 (-C-(CO)-O-).

2.2 Synthesis of PEU random copolymers. The PEUs were synthesized by polycondensation between the diamine monomer and phosgene either in a dichloromethane solution, or in an oil-in-water emulsion. For solution polycondensation, the diamine monomer (in total: 14.00 mmol, 1.00 mol. equiv.), DMAP (42.00 mmol, 3.00 mol. equiv.) and dichloromethane (80 mL) were added to a

round bottom flask and stirred for 0.5 h under room temperature. Then, triphosgene (4.76 mmol, 0.34 mol. equiv.) was dissolved in 20 mL dichloromethane and quickly added into the flask. The reaction solution was sealed and kept at 40 °C for 10 h. Afterwards, the reacted solution was poured into hot deionized water, and tar-like raw product was collected. For interfacial polycondensation, the diamine monomer (in total: 14.00 mmol, 1.00 mol. equiv.), sodium carbonate (32.20 mmol, 2.30 mol. equiv.) and deionized water (130 mL) were added to a round bottom flask and stirred for 2 h under room temperature. Then, triphosgene (5.60 mmol, 0.40 mol. equiv.) was dissolved in 20 mL dichloromethane and quickly added into the flask under vigorous stir. After 12h of stir, the organic phase of reaction emulsion was transferred drop by drop into hot deionized water, from which soft solid was collected. The raw product was purified by dissolution in chloromethane and precipitation into ethyl acetate. After dried in a vacuum oven, white solid was obtained, and the chemical structure was characterized by ^1H NMR, ^{13}C NMR and FT-IR spectroscopies.

The composition of the PEUs was varied by changing the feed ratio between two different diamine monomers. According to the compositions, the PEU products were denoted as A_xV_{1-x} , where A, V, x and (1-x) represents the *L*-alanine, *L*-valine and the corresponding composition of each diamine monomer, respectively.

$\text{A}_{1.00}\text{V}_{0.00}$: ^1H NMR (600 MHz, $\text{DMSO-}d_6$, δ): 6.35 (d, 2H), 4.02 (m, 6H), 3.30 (s, H_2O), 2.50 (m, DMSO), 1.52 (m, 4H), 1.23 (m, 14H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, δ): 173.94, 157.08, 64.46, 48.60, 40.00 (DMSO), 29.27, 29.02, 28.53, 25.66, 18.41. FT-IR (cm^{-1}): 1562, 1634 (-NH-(CO)-NH-), 1736 (-C-(CO)-O-), 3350 (-NH-(CO)-NH-).

$\text{A}_{0.94}\text{V}_{0.06}$: ^1H NMR (600 MHz, $\text{DMSO-}d_6$, δ): 6.36 (d, 2H), 4.38-3.84 (m, 6H), 3.30 (s, H_2O), 2.50 (m, DMSO), 2.10-1.85 (m, 2H), 1.59 (m, 4H), 1.38-1.06 (m, 14H), 0.83 (m, 12H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$, δ): 173.96, 157.11, 64.63, 48.61, 40.00 (DMSO), 29.28, 29.04, 28.54, 25.67, 18.40. FT-IR (cm^{-1}): 1556, 1637 (-NH-(CO)-NH-), 1736 (-C-(CO)-O-), 3337 (-NH-(CO)-NH-).

A_{0.72}V_{0.28}: ¹H NMR (600 MHz, DMSO-*d*₆, δ): 6.56-6.26 (m, 2H), 4.32-3.80 (m, 6H), 3.35 (s, H₂O), 2.50 (m, DMSO), 1.97 (m, 2H), 1.54 (m, 4H), 1.36-1.08 (m, 14H), 0.83 (m, 12H). ¹³C NMR (126 MHz, DMSO-*d*₆, δ): 173.95, 157.11, 64.58, 58.11, 48.65, 40.00 (DMSO), 30.87, 29.28, 29.02, 28.47, 25.71, 19.36, 18.43, 18.10. FT-IR (cm⁻¹): 1555, 1637 (-NH-(CO)-NH-), 1733 (-C-(CO)-O-), 3336 (-NH-(CO)-NH-).

A_{0.47}V_{0.53}: ¹H NMR (600 MHz, DMSO-*d*₆, δ): 6.53-6.19 (m, 2H), 4.28-3.86 (m, 6H), 3.43-3.17 (s, H₂O), 2.50 (m, DMSO), 2.07-1.87 (m, 2H), 1.58 (m, 4H), 1.40-1.05 (m, 14H), 0.92-0.71 (m, 12H). ¹³C NMR (126 MHz, DMSO-*d*₆, δ): 172.83, 157.47, 64.58, 58.09, 48.64, 40.00 (DMSO), 30.87, 29.25, 29.01, 28.54, 25.70, 19.38, 18.44, 18.08. FT-IR (cm⁻¹): 1554, 1634 (-NH-(CO)-NH-), 1732 (-C-(CO)-O-), 3334 (-NH-(CO)-NH-).

A_{0.32}V_{0.68}: ¹H NMR (600 MHz, DMSO-*d*₆, δ): 6.34 (m, 2H), 4.27-3.86 (m, 6H), 3.47-3.12 (s, H₂O), 2.50 (m, DMSO), 1.98 (m, 2H), 1.54 (m, 4H), 1.41-1.09 (m, 14H), 0.87 (m, 12H). ¹³C NMR (126 MHz, DMSO-*d*₆, δ): 172.83, 157.94, 64.57, 58.13, 48.67, 40.00 (DMSO), 30.87, 29.25, 29.01, 28.55, 25.70, 19.38, 18.44, 18.08. FT-IR (cm⁻¹): 1554, 1634 (-NH-(CO)-NH-), 1732 (-C-(CO)-O-), 3334 (-NH-(CO)-NH-).

A_{0.12}V_{0.88}: ¹H NMR (600 MHz, DMSO-*d*₆, δ): 6.54-6.24 (m, 2H), 4.17-3.87 (m, 6H), 3.50-3.27 (s, H₂O), 2.50 (m, DMSO), 1.98 (m, 2H), 1.57 (m, 4H), 1.40-1.05 (m, 14H), 0.92-0.64 (m, 12H). ¹³C NMR (126 MHz, DMSO-*d*₆, δ): 172.83, 157.94, 64.52, 58.13, 48.67, 40.00 (DMSO), 30.87, 29.24, 28.98, 28.55, 25.73, 19.38, 18.46, 18.08. FT-IR (cm⁻¹): 1550, 1635 (-NH-(CO)-NH-), 1735 (-C-(CO)-O-), 3352 (-NH-(CO)-NH-)

3. Supplementary figure

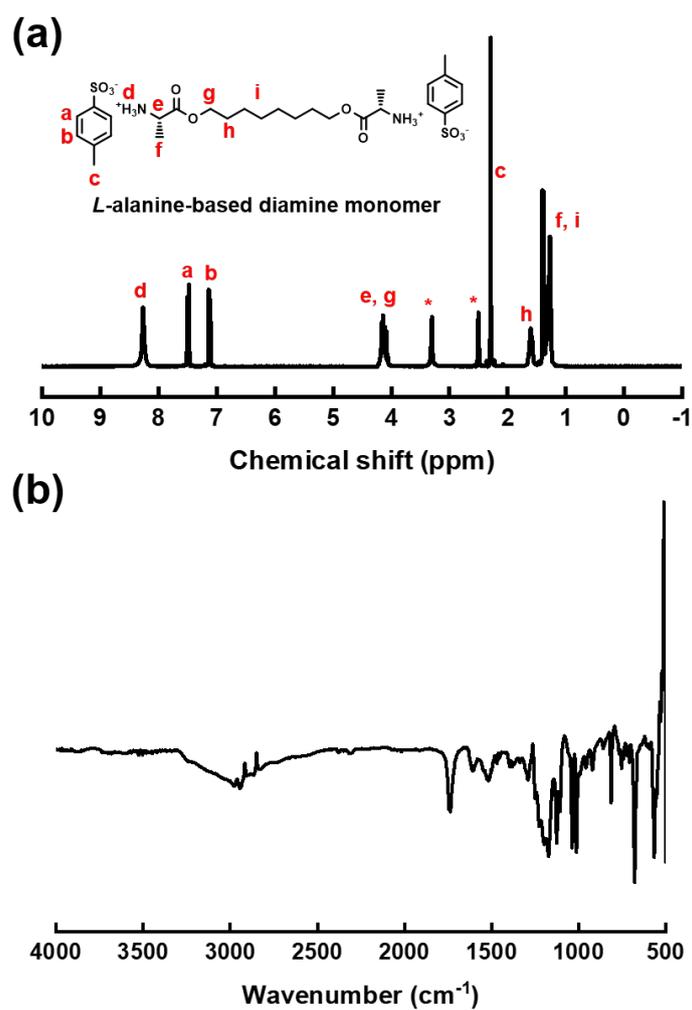


Figure S1. (a) ¹H-NMR and (b) FT-IR spectra of *L*-alanine-based diamine monomer. Peaks labeled by * in (a) represent DMSO and water.

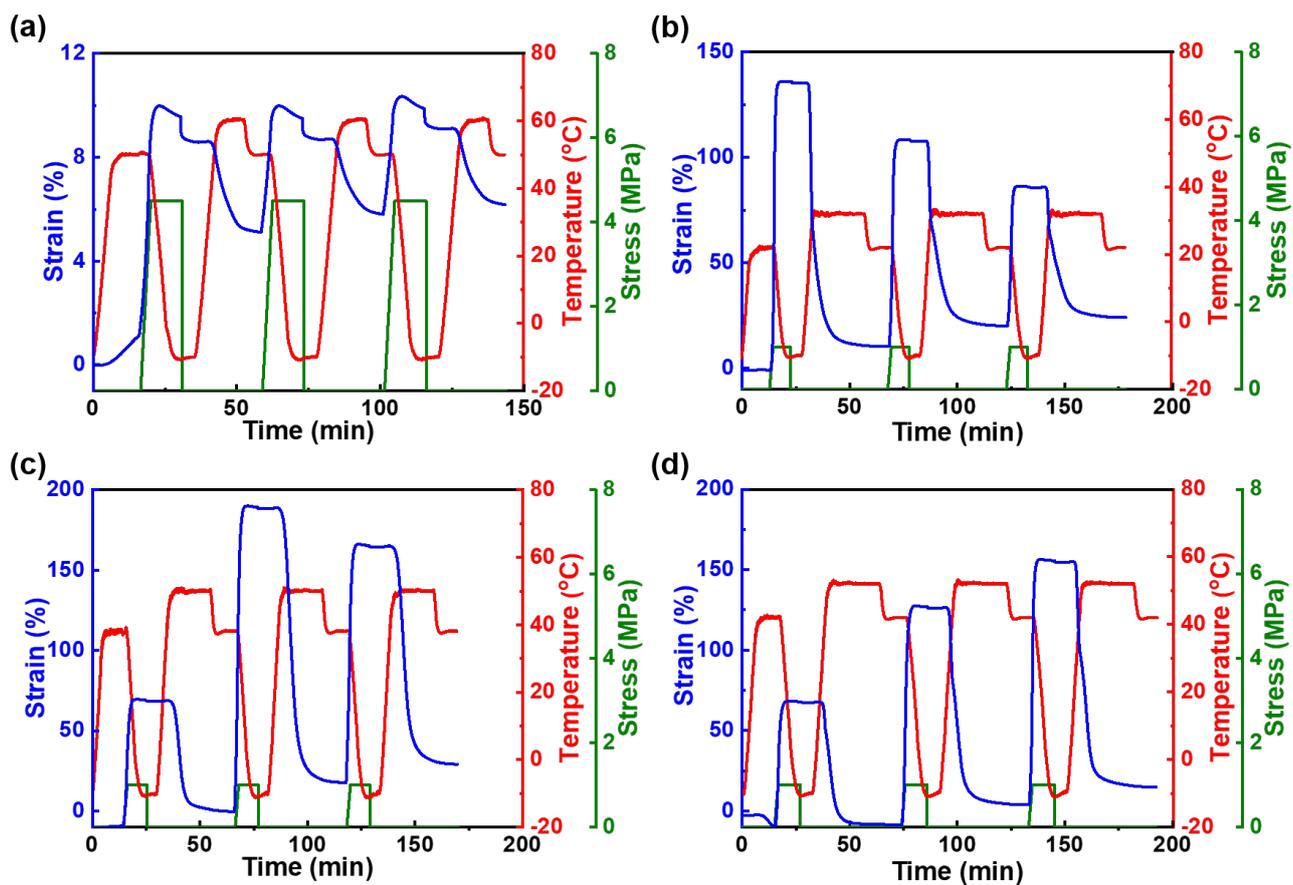


Figure S2. Representative figures of the three-cycle shape memory characterizations for (a) $A_{0.94}V_{0.06}$, (b) $A_{0.72}V_{0.28}$, (c) $A_{0.32}V_{0.68}$ and (d) $A_{0.12}V_{0.88}$ PEU thin films. For $A_{0.94}V_{0.06}$, the specimen was programmed at a T_{high} of 50 °C by a stress of 4.5 MPa in each cycle. For $A_{0.72}V_{0.28}$, $A_{0.32}V_{0.68}$ and $A_{0.12}V_{0.88}$, the specimens were programmed at a T_{high} equal to T_g by a stress of 1.0 MPa.