New Journal of Chemistry

Electronic Supplementary Information

New Star-Shape Memory Polyurethane capable of thermal-induced recovery and hydrogen bond-Self Healing

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Zonghui Huang, Jianfeng Ban*, Lulu Pan, Shuqing Cai, Junqiu Liao*

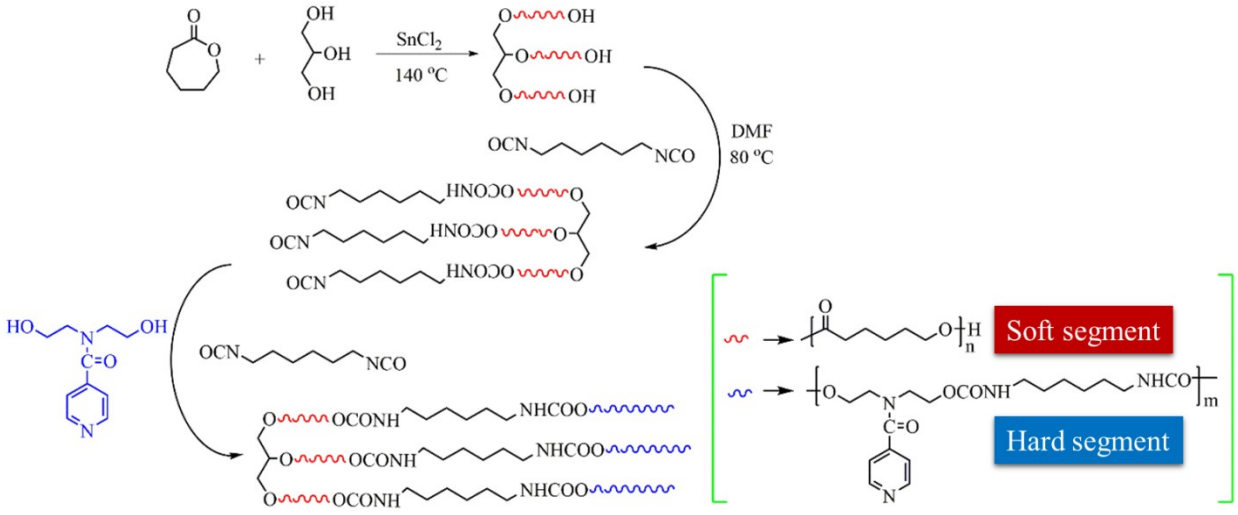
Experimental section

Materials. All reagents were purchased and used without purification.

Synthesis. Star-Shaped Poly(ε-caprolactone) (3SPCL) was synthesized by the ring-opening polymerization method. First, a certain amount of 27.9 g of ε-CL, 0.5 g of Gl, and 0.1 g of $SnCl_2$ were added into a 250 mL three flask. Then the polymerization was carried out at 140 °C for 6 h. After cooled to room temperature, the product was dissolved in 25 mL of CH_2Cl_2 and precipitated in 800 mL of cold ethyl alcohol. Finally, the resulting precipitate was dried under a vacuum at 30 °C for 8 h to obtain the target polymers 3SPCL. The Star-Shaped Memory Polyurethane (3-SMPUn) were synthesized via solution polymerization with 3SPCL, BIN, and HDI. Using the synthesis of P1 as a model case, polymerization was started by adding 5.0 g of 3SPCL, 0.52 g of HDI, and 16 mL of DMF to a 250 mL conical flask equipped with a mechanical stirrer. This pre-polymer was constantly stirred at 80 °C for 1 h. And then, 0.62 g of BIN, 0.79 g of HDI, and 6 mL of DMF were added to the reaction mixture, which was then stirred for an additional 4 h. After stopping the reaction, 5 mL of ethanol was added drop wise into the flask. The resulting pre-polymer was then poured into a Teflon pan and post-cured at 80 °C for 24 h to obtain the target 3-SMPUn. The samples were coded as P1-P5 (3-SMPUn, n = 2.0, 2.5, 3.0, 3.5, and 4.0, which is the molar ratio of BIN/3-SPCL).

Measurements. FT-IR spectra were scanned from smooth 0.2 mm thick polymer films using a Nicolet 760 FT-IR spectrometer by according to the FT-IR attenuated total reflection (ATR) method. Ten scans at a resolution of 4 cm-1 were signal averaged and stored for further analysis. XRD experiments were performed using a BRUKER AXS D8 Advance diffractometer with a 40 kV FL tube as the X-ray source (Cu Kα) and a LYNXEYE-XE detector. DSC was performed using a NETZSCH DSC214 instrument with nitrogen as the purged gas. Indium and zinc standards were used for calibration. Samples were first heated from 30 °C to 150 °C at a heating rate of 10 °C/min and kept at 160 °C for 2 min, subsequently, cooled to -20 °C at a cooling rate of 10 °C/min, and finally heated a second time from -20 °C to 160 °C. TGA curves were recorded on a computer-controlled NETZSCH Instrument TG209F3 system, under the following operational conditions: a heating rate of 10 °C/min, a temperature range of 35-600 °C, a sample weight of approximately 5.0 mg, using film samples in platinum crucibles, and 60 mL/min N2 flow. Three or four repeated readings (temperature and weight loss) were made for the same TG curve, and each included to at least 15 points. DMA curves were determined utilizing a DMA242E system (NETZSCH) at a heating rate of 2 °C min^{-1} under 1 Hz. The measured samples were cut into rectangle shape with a thickness of 0.5 mm.

Supplementary tables and figures



Scheme S1 Synthetic route of 3-SMPUn

Table S1 Composition of the 3-SMPUn.

Sample	Pre-polymer		Chain Extender	
	3SPCL (g)	HDI (mL)	BIN (g)	HDI (mL)
P1	5.00	0.52	0.62	0.79
P2	5.00	0.52	0.85	1.02
P3	5.00	0.52	1.12	1.29
P4	5.00	0.52	1.42	1.59
P5	5.00	0.52	1.78	1.94

Table S2 Thermal properties of the 3-SMPUn.

Sample	T_{d1} (°C)[a]	T_{d2} (°C)[a]	T_m (°C)[b]	T_g (°C)[b]	Tensile strength (MPa)	DPSATR (%)[d]
P1	214.9	402.0	53.5	128.1	13.38	0.499
P2	213.8	403.1	51.7	128.6	14.25	0.497
P3	212.0	404.7	50.3	129.3	11.83	0.496
P4	210.4	415.3	48.4	129.5	11.56	0.495
P5	209.1	418.1	44.8	130.0	7.86	0.493

a. The weight loss temperatures of the samples under nitrogen [$T_d(N_2)$] were measured by TGA heating experiments at a rate of 10 °C min^{-1}.

b. Evaluated by DSC during the second heating process at a rate of 10 °C min^{-1} under nitrogen atmosphere.

c. Evaluated by

d. Degree of microphase separation (DPS_{ATR}) calculated by the equation:

$$DPS_{ATR} = \frac{C{=}O_{bonded}}{C{=}O_{bonded} + C{=}O_{free}}$$

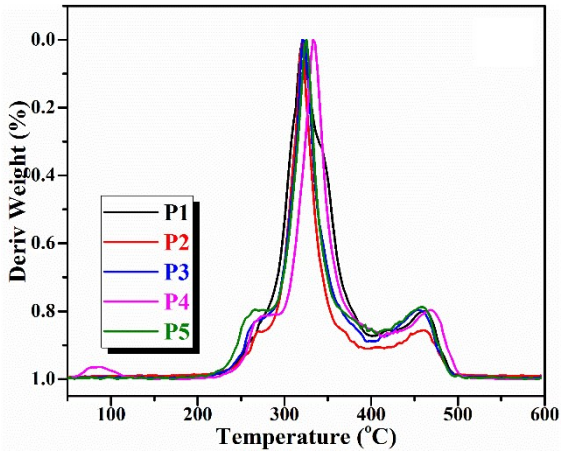


Fig. S1 Thermo-gravimetric analysis curves of the 3-SMPUn (weight loss rate with temperature).

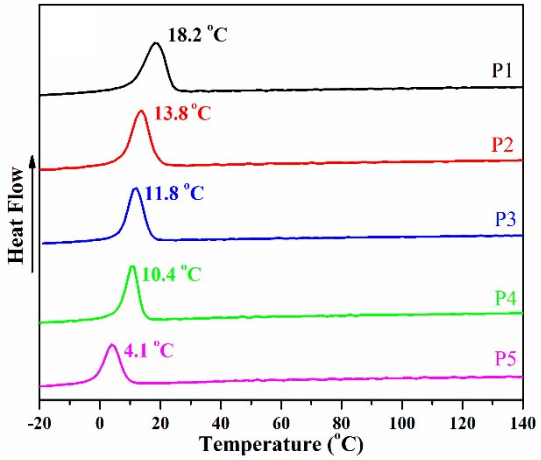


Fig. S2 DSC curves of 3-SMPUn at the first cooling run.