Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A facile preparation strategy of PCL-based biodegradable polyurethane elastomer with highly efficient shape memory effect

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Experimental Section

1.1 Materials and Methods

Dicyclohexylmethane-4,4'-diisocyanate (HMDI, 98%) was purchased from Sigma-Aldrich. PCL was purchased from XiaoGan ESUN New Material Co. Ltd (M_n=1000g mol^{-1}, T_g=-32 °C , T_m=48.5°C). The dimethyl-formamide (DMF), 1,4-butanediol (BDO) and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, 98%) were procured from Aladdin Co. Ltd.

1.2 The Characterization of PCBU and PCTU Elastomers

1.2.1 IR spectroscopy

Spectra data were collected on a **Nicolet 6700** (USA, Thermo) spectrometer in ATR mode.

1.2.2 X-ray diffraction

The X-ray diffraction results were recorded with a Bruker AXS D8 Advance, using Cu-Kα radiation (λ = 1.541 Å) in the scan range from 5 to 60° at 4° min−1. 300 μm thickness samples with equilibrium crystallinity were recorded.

1.2.3 Thermomechanical properties

Different Scanning Calorimetry (**DSC**) were carried out by **DSC 214 (Germany)**. The measurements were repeated in a temperature range of -50 °C to 150 °C at a rate of 10 °C min^{-1}and a flow of pure nitrogen was 20 mL min^{-1}.

Thermogravimetric Analysis (**TGA**) were carried out by Diamond TG/DTA **(USA)**. About 5~8 mg of sample was continuously recorded in a temperature range from 0 °C to 800 °C at a rate of 10 °C min^{-1}and a flow of pure nitrogen was 20 mL min^{-1}.

Dynamic mechanical analysis (**DMA**) was carried out by **DMA Q800 (USA),** Samples were heated from −100 °C to 100 °C with a heating ramp of 3 °C/min, at a frequency of 1 Hz and an oscillatory amplitude of 5 μm.

1.2.4 GPC and Cross-linking density

Molecular weights were measured by GPC (Agilent PL-GPC220) at 40 °C. HPLC grade DMF was used as eluent with a flow rate of 1.0 mL min−1. The test of cross-linking density refers to the methods in the literature.[1]

1.2.5 Mechanical properties

The elongation at break, tensile modulus and toughness of **PCBU** and **PCTU** were measured using an Instron 5567 tensile tester at a strain rate of 5 mm min^{-1} at room temperature. Samples were made by solvent casting, maintaining the dimension of 20× 7 ×0.8mm^3. The experiment was carried out in triplicate to obtain good error estimation.

1.2.6 Morphological investigation

The images from scanning electron microscopy (**SEM**) were captured by a S4800 (Japan, Hitachi). All the samples were sputter-coated with ∼10 nm gold using an anion sputter coater (E-1045, Hitachi) for 120 s before test, in order to improve the conductivity of the samples and the quality of the SEM images. The images from polarized optical microscope (**POM**) were captures by a BX51 (Japan, Olympus). It is used to observe and record the surface of the sample before and after degradation. The measurements were under the condition of 25°C. Atomic Force Microscope (**AFM**), controlled by a Solver scanning probe microscope controller, was used for scanning the bulk morphology of the samples. The photos were captured by **Bruker Dimension Icon.** The semi-contact mode was used with a 10 μm log, single beam cantilever on which a tip was mounted with a resonant frequency range of 200 to 300 kHz with the corresponding spring constant of 40 N m^{-1}. The measurements were under the condition of 23°C and which humidity was 42 %。

1.2.7 Triple-Shape Memory Properties

The shape memory behavior of PCBU and PCTU was checked using two different procedures. 1 mm thick standard polymeric strips were prepared through a solution casting route and were dried at 60 °C under low pressure. Quantification of the shape memory behaviour was done with the sample dimensions of 21 × 7 × 0.8 mm^3 using a uniaxial tensile tester (**DMA Q800**) with an externally attached temperature controller.

The typical thermocyclic procedure as follows：

① The sample was set under the Force= 0.001 N for 10 min, then samples were heated to 70 °C (T_{high}) by a rate of 10 °C/min,
and then was equilibrated for 10 min,

② uniaxial stretching was applied to reach a predetermined strain ($\varepsilon_{I,load}$) by ramping the force from 0.001 MPa to 0.4 MPa at a tensile speed rate of 0.2 MPa /min, and then was for equilibrated 5 min,

③The strain was fixed by sample was cooling to 55 °C (T$_g$) at a rate of 10 °C/min, followed by equilibration for 10 min,

④Then external force was unloaded to 0.001 MPa at a tensile rate of 0.2 MPa /min, and the strain was recorded as $\varepsilon_{\mathbf{fix, I}}$, The sample was equilibrated for 5 min

⑤uniaxial stretching was applied to reach a predetermined strain ($\varepsilon_{\mathrm{II, load}}$) by ramping the stress to 0.8 MPa at a tensile speed rate of 0.2 MPa /min, and then was equilibrated for 5 min,

⑥The sample was cooled to 0 °C (T$_{\mathrm{low}}$) at a rate of 10 °C/min, then the sample was equilibrated for 10 min, and the. Strain was recorded as $\varepsilon_{\mathrm{I, rec}}$,

⑦Then external force was unloaded to 0.001 N at a tensile rate of 0.2 MPa /min, and the strain was recorded as $\varepsilon_{\mathrm{fix, II}}$, The sample was equilibrated for 5 min,

⑧The samples were heated to 55 °C (T$_g$) by a rate of 10 °C/min, and the sample was equilibrated for 40 min,

⑨The sample was heated to 70 °C (T$_{\mathrm{high}}$) by a rate of 10 °C/min, uniaxial stretching was applied to reach another predetermined strain ($\varepsilon_{\mathrm{II}}$) by ramping the force from 0.001MPa to 0.8 MPa at a tensile speed rate of 0.1 MPa /min, and then was equilibrated for 40 min. Finally, the process was repeat the cycle twice.

The samples were stretched to 200 % by keeping the strain rate of 5 mm min^{-1} at the shape giving temperature (T$_{\mathrm{high}}$) and were equilibrated for 10 min. After that, cooling was done to T$_g$ for 10 min to fix the temporary shape and the applied stress was kept constant. Lastly, cooling was done to T$_{\mathrm{low}}$ for 10 min to recover the temporary shape and the applied stress was kept constant. After removing the stress, the samples were heated at T$_{\mathrm{high}}$ again to go back to their initial shapes. The shape fixity (R$_f$) and shape recovery (R$_r$) ratios were calculated using equation (1) and (2) given below:

$$R_f\ (I \rightarrow II) = \frac{\varepsilon_{II} - \varepsilon_I}{\varepsilon_{II,\ \mathrm{lood}} - \varepsilon_I} \times 100\%$$

$$R_r\left(II \rightarrow I\right) = \frac{\varepsilon_{II} - \varepsilon_{I,rec}}{\varepsilon_{II,load} - \varepsilon_I} \times 100\%$$

1.2.8 Biodegradation Properties

Bio-degradation experiments were performed in phosphate buffered solution (PBS, pH = 7.4) at 37 °C and were last for 2 months. The dimensions of PU films were 10 × 10 ×0.8 mm^3 and added them to 20 mL of PBS solutions, calculated original weight (W_0), After7 days of degradation, the films were washed and dried to fixed weight. the solutions were replaced every 7days. Calculated residual weight (W_g), then the degradation level was estimated from the percentage of weight loss ($\triangle W$), according to the following equation:

$$weight\ loss\ rate = \frac{\triangle W}{W_0} \times 100\% = \frac{W_0 - W_g}{W_0} \times 100\%$$

$$weight\ residual\ rate = \frac{W_g}{W_0} \times 100\%$$

1 S. L. Xu, Y. Y. Zhang, M. Wang, H. L. Zhao, W. Hu, *China Rubber Industry*, 2017, **10**, 624.

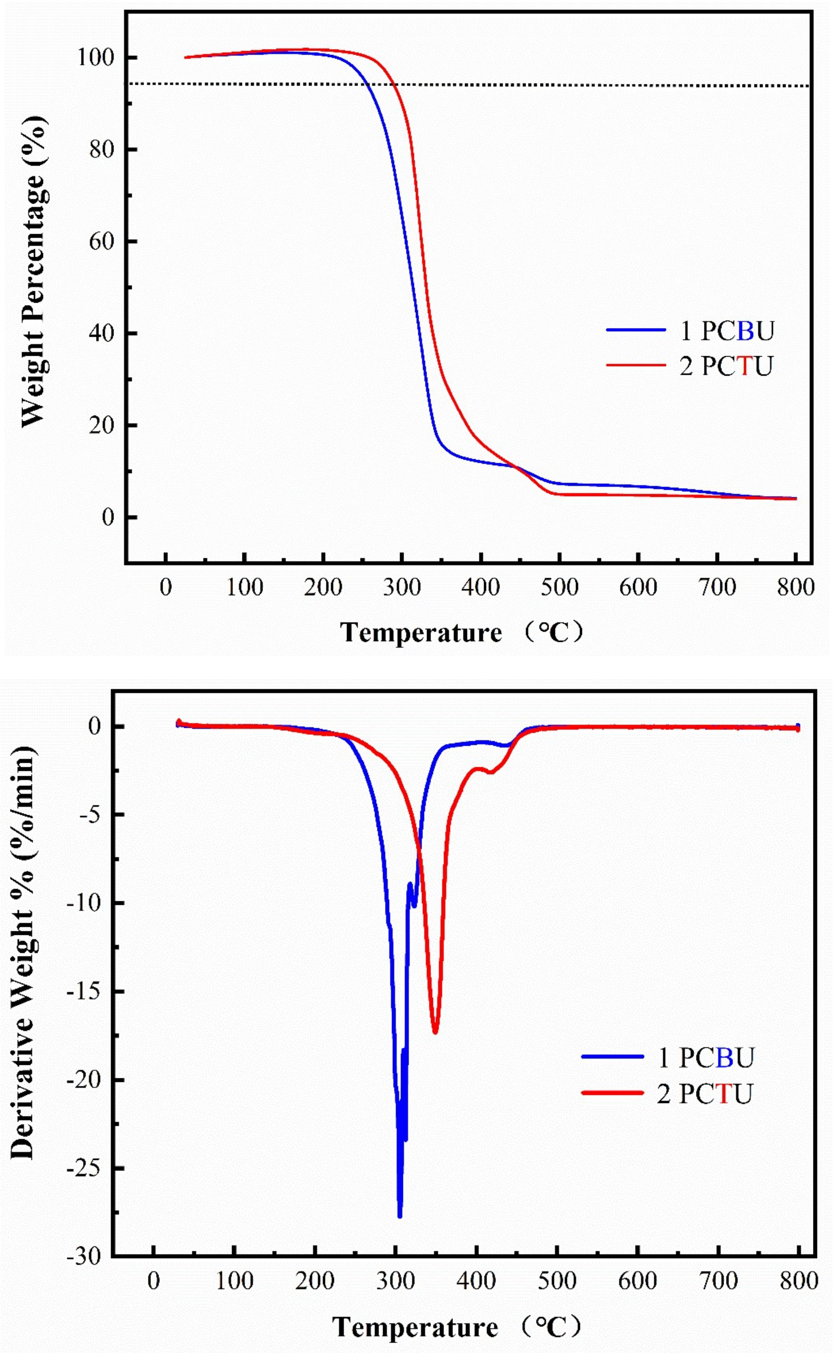

Fig. S1 TGA and DTG curves for **PCBU** and **PCTU**.

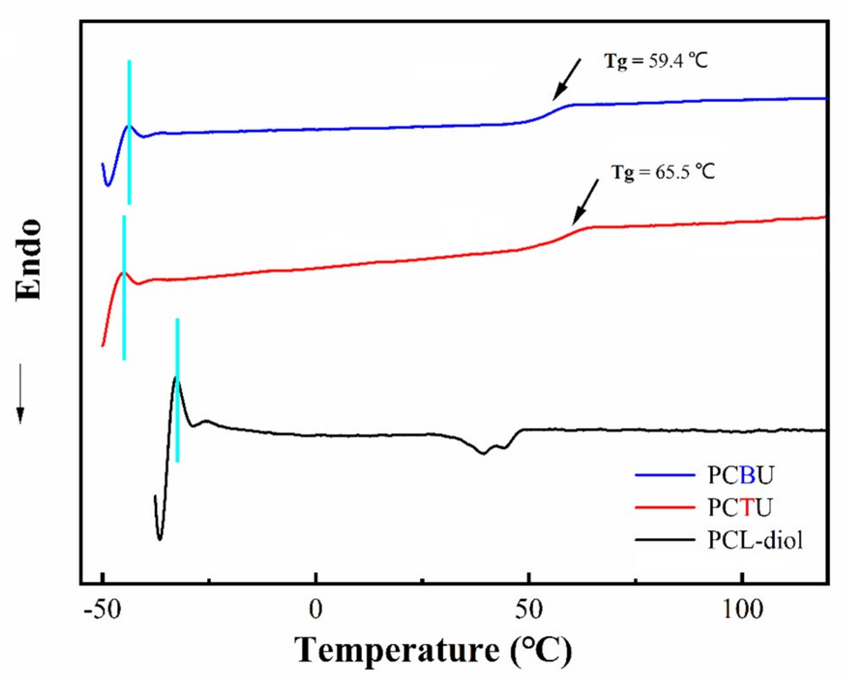

Fig. S2 DSC of **PCL-diol**, **PCBU** and **PCTU**.

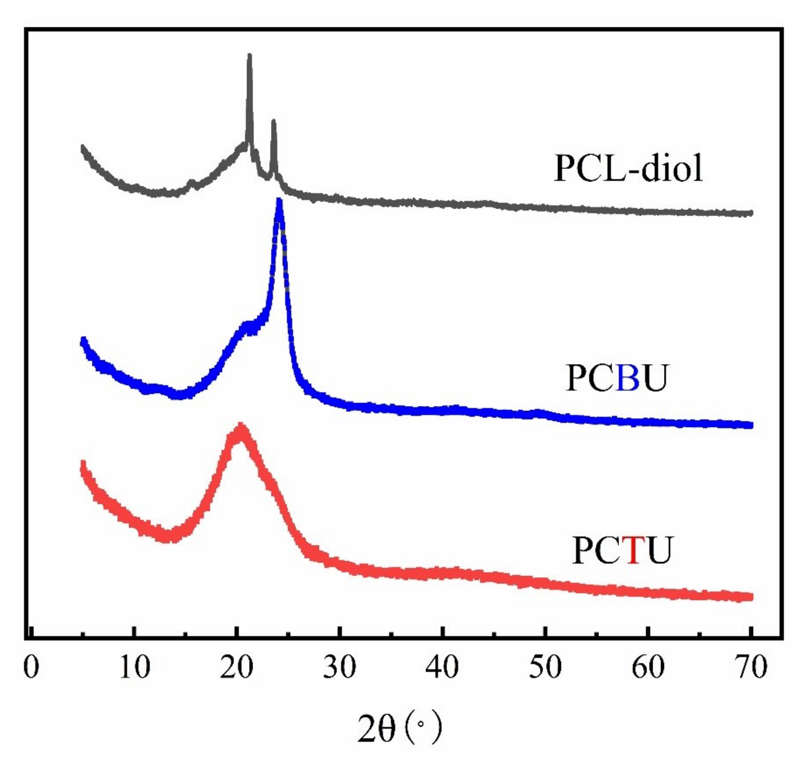

Fig. S3 X-ray diffractograms of **PCL-diol**, **PCBU** and **PCTU**.

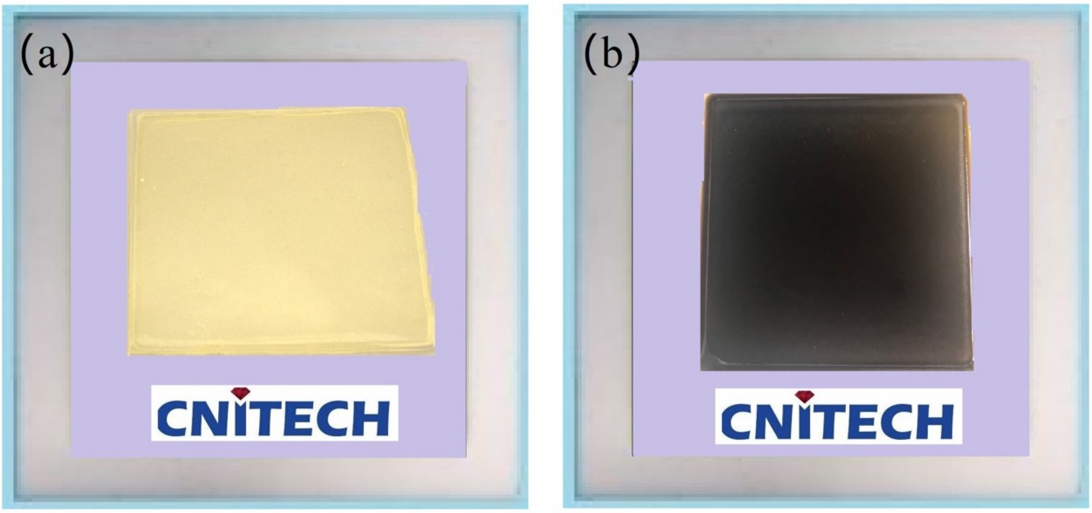

Fig. S4 The photos of (a) **PCBU** and (b) **PCTU.**

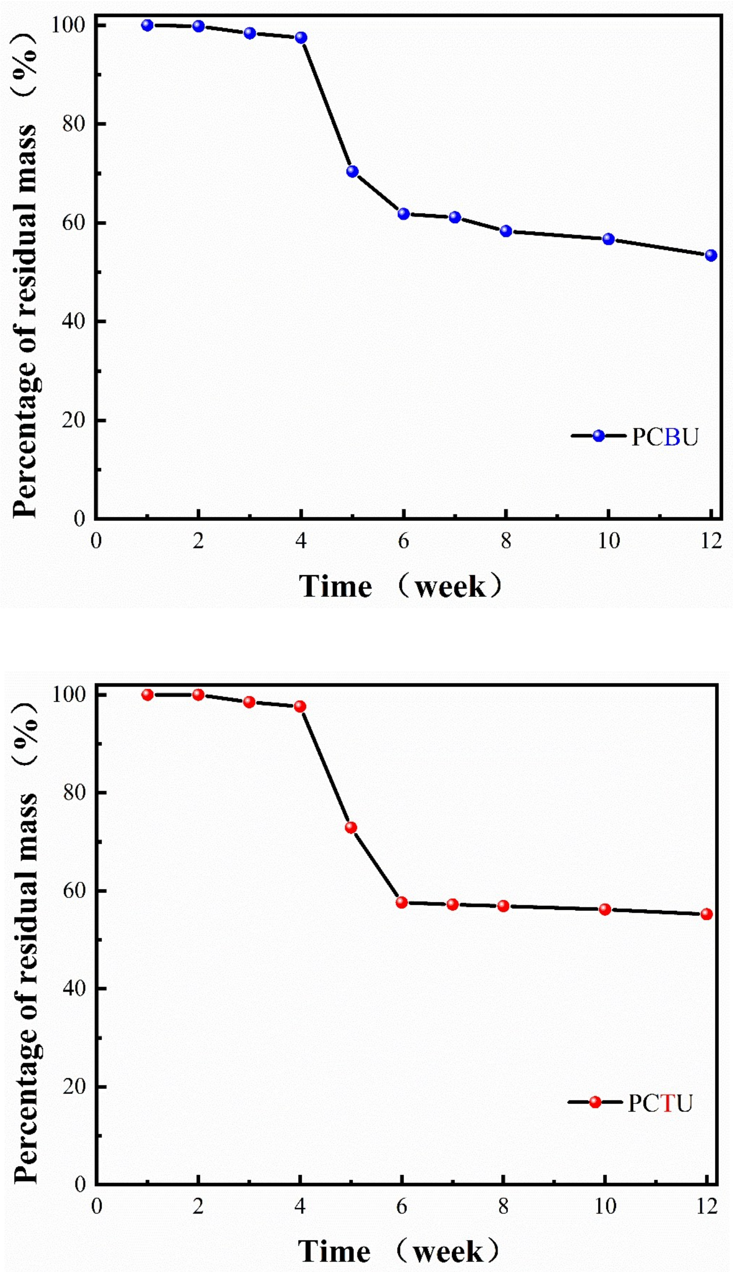

Fig. S5 (a) Residual mass curves of PCBU during hydrolysis degradation. (b) Residual mass curves of PCTU during hydrolysis degradation.

Tables

Table S1. Detailed information on the poly (PCL urethane) elastomers.

Samples	Polyol (mmol) [a]	HMDI (mmol)	R-CE (mmol)	HS (%) [b]	R [c]
PCBU	5	10	4	37.6	1.1
PCTU	5	10	4	44.3	1.1

[a] Polyol: [PCL] and its M_n 1000, chain extender: **PCBU**:1,4-butanediol (**BDO**), **PCTU**: 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindan (**TTSBI**). [b] contents of hard segment(weight); [c] the ratio of [-NCO] / [-OH].

Table S2. Thermal properties of poly (PCL urethane) elastomers.

Samples	T_g^{DSC} (℃) [a]	T_d (℃) [b]	T_α (℃) [c]
PCBU	59.4	252	-36.2
PCTU	65.6	286	-37.3

[a] Glass transition temperatures as determined from the DSC runs;

[b] Decomposition temperature recorded at 5% weight loss at the TGA thermograms；

[c] Maximum α relaxation temperature obtained on the Tanδ-temperature curves;

Table S3. Mechanical properties of poly (PCL urethane) elastomer.

Samples	*E* (MPa) [a]	σ_b (MPa) [b]	ε_b (%) [c]
PCBU	12.4±0.6	16.6±3.2	516±23
PCTU	19.1±1.4	20.4±2.3	594±40

[a] Young's modulus; [b] Stress at break; [c] Strain at break;

Table S4. Shape fixity and recovery properties of poly (PCL urethane) elastomers.

Samples	R_{f1} (%)	R_{f2} (%)	R_{r1} (%)	R_{r2} (%)	R_{r3} (%)
PCBU	0.725	0.911	0.950	0.992	0.851
PCTU	0.738	0.993	0.982	0.994	0.983

Table S5. Cross-linking density and molecular weight of poly (PCL urethane) elastomers.

Samples	Before degradation	After degradation
PCTU	6.34×10^{-4} mol ● cm^{-3}	3.12×10^{-5} mol ● cm^{-3}
PCBU	1.2×10^4 kDa	0.5×10^4 kDa