Supplementary Information

High-strain Slide-Ring Shape Memory Polycaprolactone-based Polyurethane

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The PEG ditosylates:

Polyethylene glycol (PEG, M_w = 20 000 g/mol) (5.0 g, 0.250 mmol) was dissolved in CH_2Cl_2 (30 mL) in a round-bottomed flask. The mixture was stirred for 10 min. p-TsCl (1.0 g, 10 mmol) and dimethylamino-pyridine (25 mg, 0.2 mmol) were then introduced into the solution. The reaction was stirred overnight, then concentrated to 5 mL and added dropwise to diethyl ether. The white precipitate was collected by filtration. The white precipitate was dried at room temperature under vacuum for 3 days.
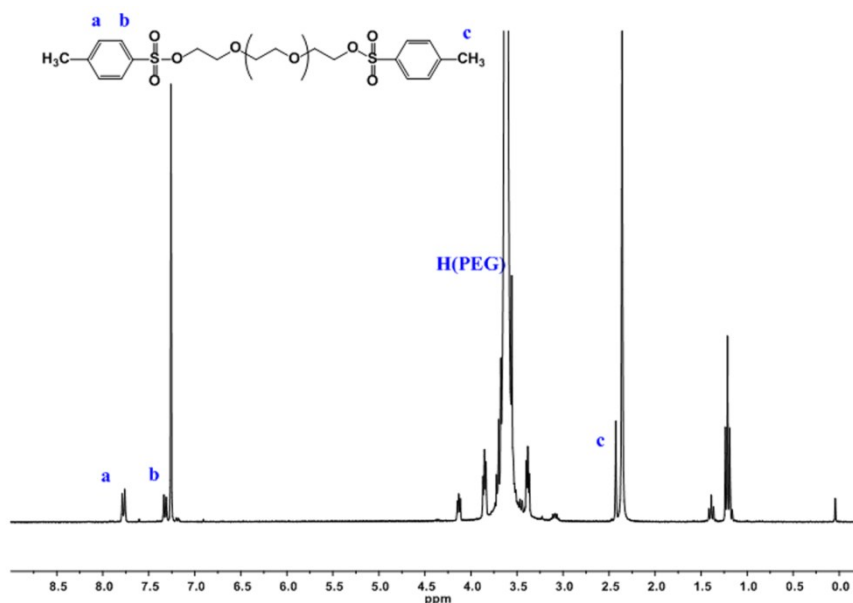
Figure S1. ^{1}H NMR spectra of bis-tosyl-terminated PEG in CDCl$_3$.

The α,ω-ditosyl-terminated PEG polypseudorotaxanes:

An α-CD aqueous solution (1 g, in 7 mL of H$_2$O) was combined with an aqueous solution of bis-tosyl-terminated PEG (1 g, in 5 mL H$_2$O) at room temperature. The clear mixed solution became turbid within 30 min and was allowed to stand overnight at 5 ℃. Sticky mixture was freeze-dried to obtain the polypseudorotaxanes.
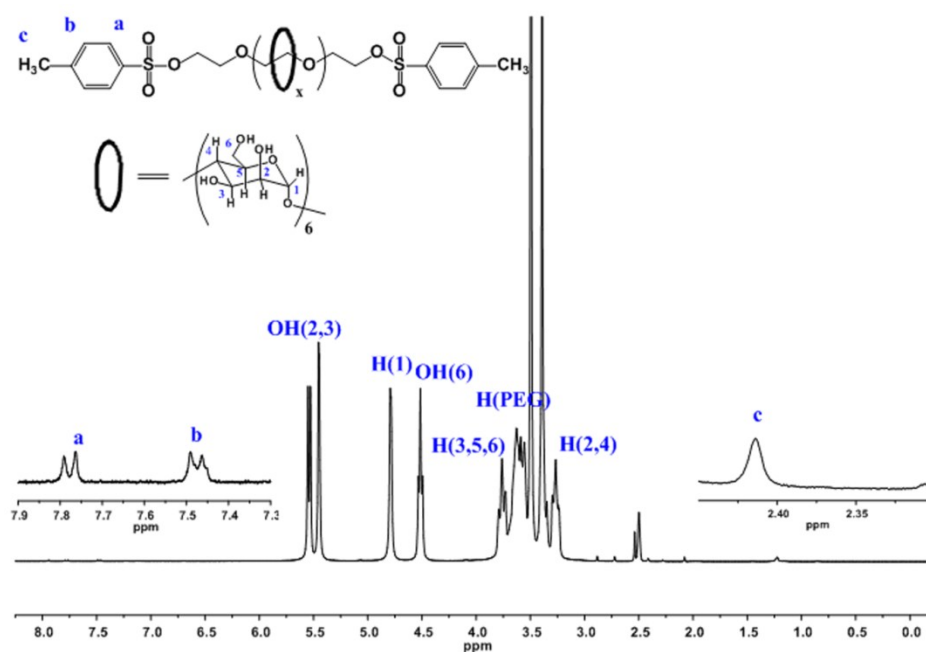

Figure S2. ^{1}H NMR spectra of the α,ω-ditosyl-terminated PEG polypseudorotaxanes in DMSO-d$_6$.

PEG polyrotaxanes:

A solution of 3, 5-dimethylphenol (0.86 g, 7.0 mmol) in DMF (10 mL) was slowly added to dry NaH (0.25 g) in a round-bottomed flask under a strong argon purge. The α,ω-ditosyl-terminated PEG polypseudorotaxanes (1.0 g) was then added to the reaction flask and rinsed down with 4 mL of DMF. After stirring overnight, the reaction mixture was poured into 60 mL of methanol. The precipitate was collected by filtration, washed with 2 × 20 mL of methanol, dissolved in 6 mL of DMSO, and precipitated into 50 mL of methanol. The precipitate was again collected by filtration and washed with 2 × 20 mL of methanol. Finally, the white solid product was dried at 110 °C overnight under vacuum.
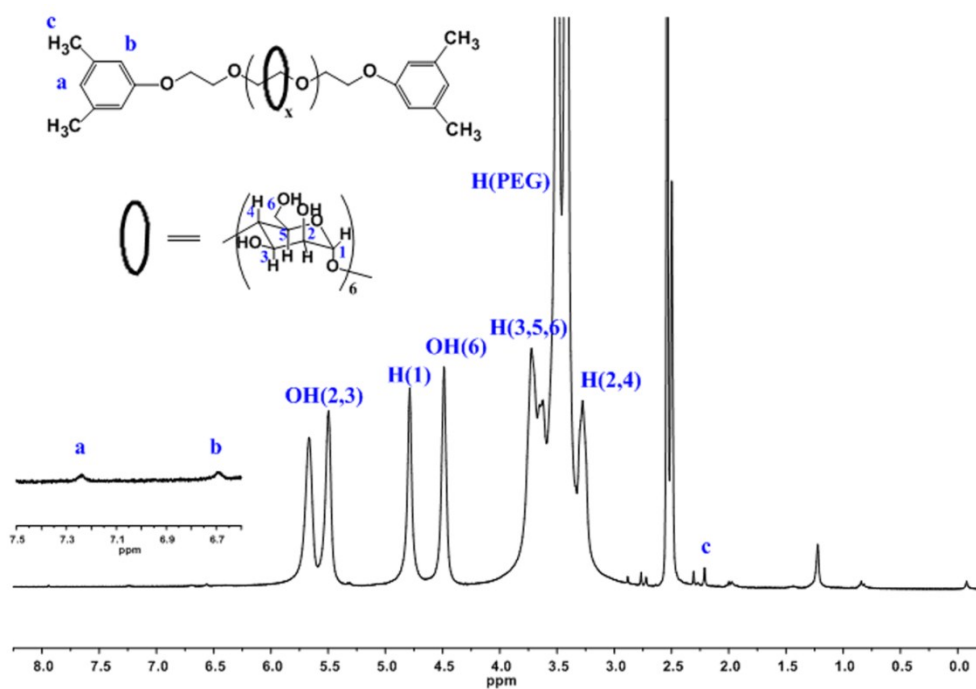

Figure S3. ^{1}H NMR spectra of PEG polyrotaxanes in DMSO-d_6 with TMS as an internal standard.
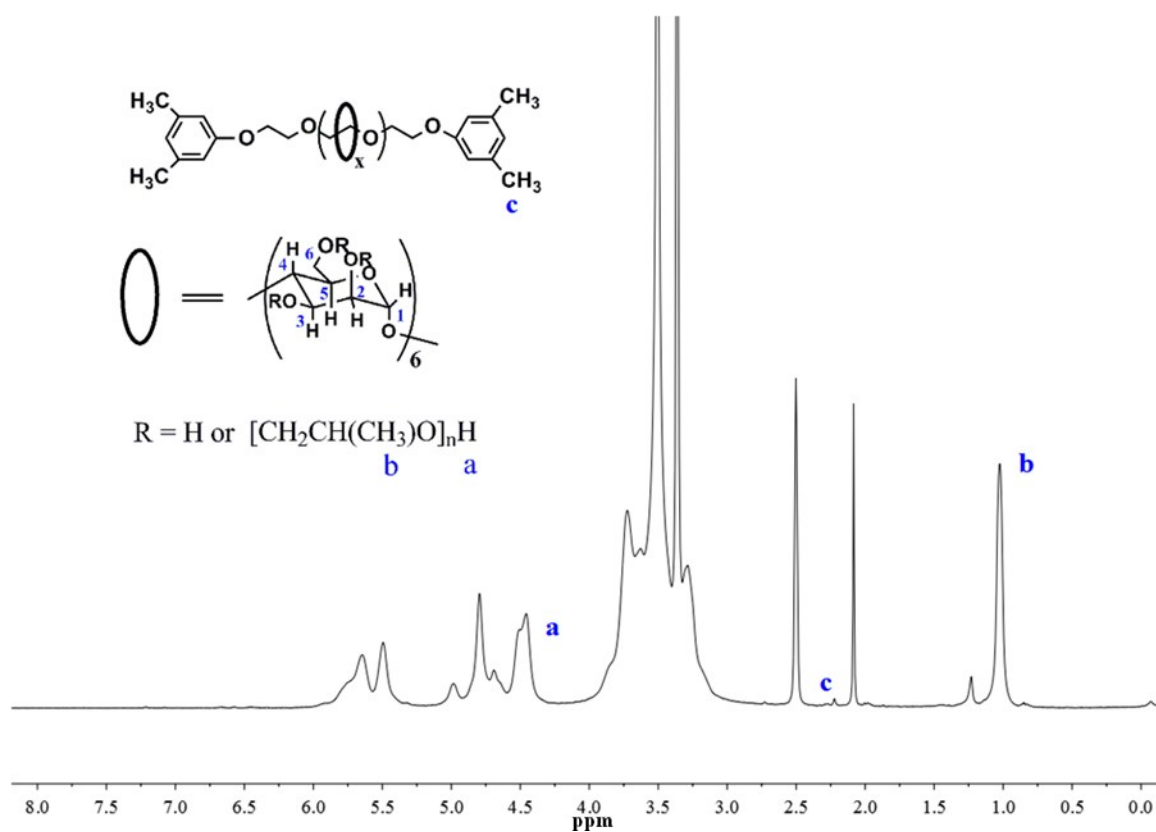
Figure S4. ^{1}H-NMR spectra of HPPR in DMSO-d_6 with TMS as an internal standard.
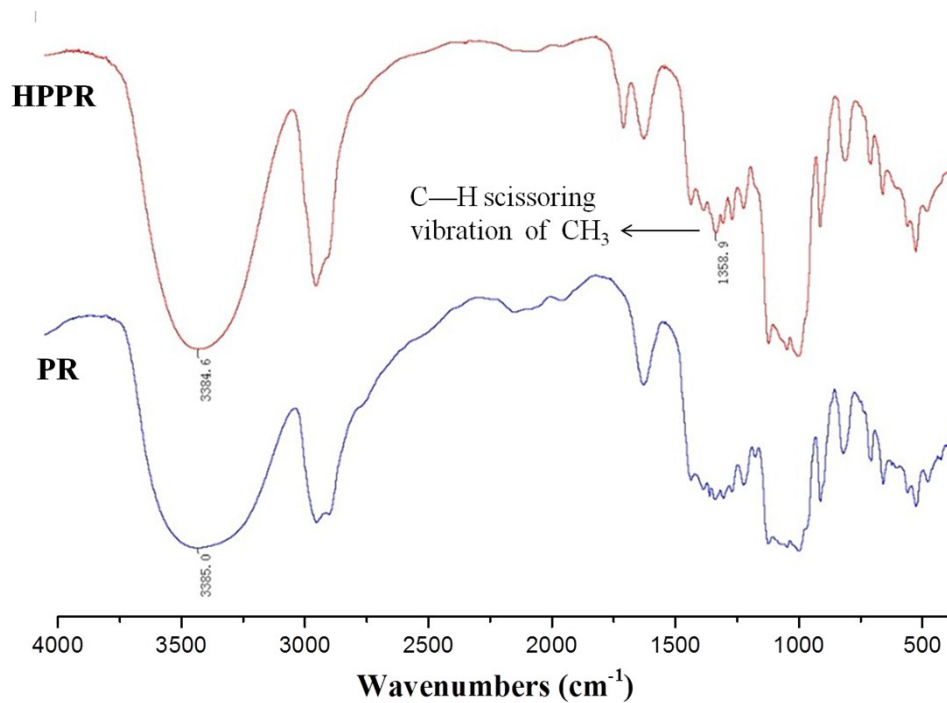

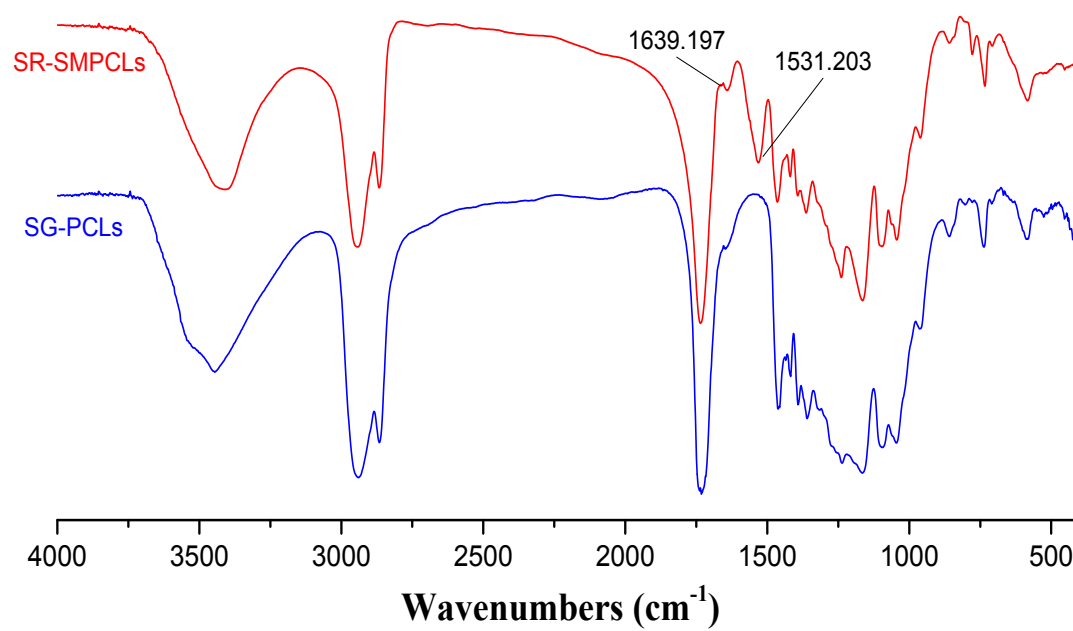**Figure S5.** FT-IR spectra of PR and HPPR

Figure S6. FT-IR spectra of sliding graft PCL (SG-PCLs) and slide-ring PUs (SR-SMPCLUs)

Table S1. Measured SME Parameters of the samples at different deformation strains

Sample	Strain	ε_n (%)	ε_m (%)	ε_u (%)	ε_p (%)	R_f (%)	R_r (%)	V_r (%/min)
SR-SMPCLU	20%	0.169	21.40	21.17	0.642	**98.92**	97.43	46.01
	40%	0.205	43.24	42.90	1.439	**99.21**	97.11	36.23
	70%	0.46	65.24	64.88	0.66	**99.44**	99.69	33.04
	100%	0.686	101.137	99.817	1.012	**98.68**	99.67	32.05
	200%	0.325	215.80	213.00	1.305	**98.70**	99.54	25.00
	300%	0.35	281.44	279.44	4.54	**98.78**	99.40	20.33
	400%	0.212	376.38	374.38	2.20	**99.47**	99.41	17.99
	600%	0	600	593.5	7.33	**98.92**	98.76	
	800%	0	800	788.2	21.20	**98.53**	97.31	
	1000%	0	1000	985.4	30.25	**98.54**	96.93	
	1300%	0	1300	1287.7	44.17	**99.05**	96.57	
CC-SMPCLU	100%	0.3159	108.65	102.53	10.76	**94.35**	89.78	
	400%	1.2636	434.6	410.1	104.52	**94.35**	74.74	
	700%	0	663	636.94	140.38	**96.07**	77.96	
L-PCLU	50%	0.213	52.78	51.07	4.55	**96.61**	91.60	
	200%	0.52	256.90	255.7	58.91	**99.53**	77.12	
	800%	0	795	786.7	207.6	**98.96**	73.61	

Table S2. Measured SME Parameters of the sample SR-SMPCLUs repeated for four cycles when ε_m was about 40%

Cycle	ε_n(%)	ε_m(%)	ε_u(%)	ε_p(%)	R_f (%)	R_r (%)	$R_{r.adj}$ (%)	V_r(%/min)
1	0.316	40.49	40.15	0.862	**99.15**	98.63	98.63	38.07
2	0.862	43.94	43.6	1.584	**99.21**	98.31	97.07	35.71
3	1.584	46.17	45.95	2.574	**99.51**	97.77	95.05	41.67
4	2.574	48.759	48.549	3.238	**99.55**	98.56	93.94	38.27

Table S3. Measured SME Parameters of the sample SR-SMPCLUs repeated for six cycles when ε_m was about 280%

Cycle	ε_n(%)	ε_m(%)	ε_u(%)	ε_p(%)	R_f (%)	R_r (%)	$R_{r.adj}$ (%)	V_r(%/min)
1	0.71	278.60	273.30	9.50	**98.09**	**96.78**	**96.78**	**7.03**
2	9.50	287.39	284.09	10.01	**98.81**	**99.81**	**96.72**	**20.27**
3	10.01	280.03	278.63	10.88	**99.81**	**99.68**	**96.34**	**20.27**
4	10.88	292.02	290.02	12.78	**99.29**	**99.32**	**95.83**	**20.27**
5	12.78	271	268.7	13.57	**99.11**	**99.69**	**95.20**	**20.66**
6	13.57	291.87	289.97	15.47	**98.96**	**99.67**	**94.90**	**20.27**

Table S4. Measured SME Parameters of the sample L-PCLU repeated for four cycles
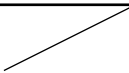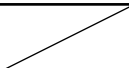
Cycle	ε_n(%)	ε_m(%)	ε_u(%)	ε_p(%)	R_f (%)	R_r (%)	$R_{r.adj}$ (%)	V_r(%/min)
1	0.52	256.90	255.7	58.91	**99.53**	**77.12**	**77.12**	
2	58.91	280.00	277.74	84.63	**98.98**	**88.25**	**69.66**	**8.09**
3	84.63	310.45	310.17	111.26	**99.87**	**88.19**	**64.24**	**8.03**
4	111.26	343.90	343.62	138.74	**99.88**	**84.57**	**59.71**	**8.09**

Table S5. Measured SME Parameters of the sample CC-SMPCLU repeated for four cycles

Cycle	ε_n(%)	ε_m(%)	ε_u(%)	ε_p(%)	R_f (%)	R_r (%)	$R_{r.adj}$ (%)	V_r(%/min)
1	0.76	259.8	246.1	51.9	**94.70**	**79.15**	**79.15**	
2	51.9	273.80	258.24	82.51	**92.99**	**85.17**	**68.25**	**8.56**
3	82.51	298.69	288.32	117.50	**95.20**	**83.00**	**59.40**	**9.57**
4	117.50	338.62	327.25	139.03	**94.86**	**89.94**	**57.65**	**11.54**

Supplementary Video S1

Actual observation of the shape recovery of panda pattern film made of SR-SMPCLU

from a stretched temporary shape to permanent shape at preset 65 °C water bath

within 1 second.