Electronic Supplementary Material (ESI) for RSC Advances.

Shape Memory Copolymer based on 2-(Dimethylamino) Ethyl Methacrylate and Methyl Allyl Polyethenoxy Ether for Potential Biological Applications

Yangyang, Chen[&a], Funian Mo[&a], Shaojun Chen[a], Yan Yang[a], Shiguo Chen[a]，Haitao Zhuo*[b], Jianhong Liu[b]；*

[a]*Shenzhen Key Laboratory of Special Functional Materials, Nanshan District Key Lab for Biopolymers and Safety Evaluation, College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518060, China.* [b]*College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen, 518060, China.*

*Corresponding author: College of Materials Science and Engineering，Shenzhen University, Shenzhen 518060, China. Tel and Fax: +86-755-26534562. E-mail: Shaojun Chen，chensj@szu.edu.cn Shiguo Chen csg@szu.edu.cn

[&] Yangyang, Chen and Funian Mo are equal contributor to this work

Supporting Information

Test 1: Shape Memory Behavior Testing

The temperature-induced shape-memory behaviors were determined with cyclic thermo-mechanical analysis using a DMA800 instrument (tension clamp, controlled force mode). All samples were dried at 100°C *in vacuo* for 24h and cut in rectangular pieces of approximately 10mm×2.0mm×0.5mm.

The test setups

1) For dual-shape-memory cycles: (1) heating to 90 and equilibrated for 20 min; (2) uniaxially stretching to strain (ε_{load}) by ramping force from 0.001N to 1N at a rate of 0.25N/min; equilibration for 3 min; (3) fixing the strain (ε) by quickly cooling to ca. 20°C with cooling rate (q) of -10°C/min, followed by equilibration for 10min; (4) unloading external force 0N at a rate of 0.25N/min; (5) reheating to ca.90°C at a rate of 4°C/min and followed by equilibration for 40min; the recovery strain (ε_{rec}) is finally recorded.

2) For triple-shape-memory cycles: (1) heating to ca. 110°C and equilibrated for 20 min; (2) uniaxially stretching by ramping force from 0.001N to 1N at a rate of 0.25N/min; equilibration for 3 min; (3) fixing the strain by quickly cooling to 70°C with q=-10°C/min, followed by equilibration for 10min; (4) further fixing the strain by quickly cooling to 20°C with q=-10°C/min, followed by equilibration for 10min; (5) unloading external force 0N at a rate of 0.25N/min; (6) reheating to 70°C at a rate of 4°C/min and followed by equilibration for 40min; (7) reheating to ca. 110°C at a rate of 4°C/min and followed by equilibration for 40min.

3) For multi-staged strain recovery cycles: (1) heating to 110°C and equilibrated for 20 min; (2) uniaxially stretching by ramping force from 0.001N to 1N at a rate of 0.25N/min; equilibration for 3 min; (3) fixing the strain by quickly cooling to 20°C with q=-10°C/min, followed by equilibration for 10min; (4) unloading external force 0N at a rate of 0.25N/min; (7) reheating to 70°C at a rate of 4°C/min and followed by equilibration for 40min. (8) further reheating to 90°C at a rate of 4°C/min and followed by equilibration for 40min. (9) further reheating to 110°C at a rate of 4°C/min and followed by equilibration for 40min.

Calculations of shape memory behaviors

For dual-shape memory effect, the shape fixity (R_f) and shape recovery (R_r) were calculated using equations (1) and (2) below:

$$R_f=100\%\times\varepsilon/\varepsilon_{load} \quad (1)$$

$$R_r=100\%\times(\varepsilon-\varepsilon_{rec})/\ \varepsilon \quad (2)$$

Where ε_{load} represents the maximum strain under load, ε is the fixed strain after cooling and load removal, and ε_{rec} is the strain after recovery.

For triple-shape memory effects, equations (1) and (2) are expanded to equations (3) and (4)

$$R_f(X\rightarrow Y)=100\%\times(\varepsilon_y-\varepsilon_x\ )/(\varepsilon_{y,load}-\varepsilon_x) \quad (3)$$

$$R_r(Y\rightarrow X)=100\%\times(\varepsilon_y-\varepsilon_{x,rec}\ )/(\varepsilon_y-\varepsilon_x) \quad (4)$$

Where X and Y denote two different shapes, respectively, $\varepsilon_{y,load}$ represents the maximum strain under load, ε_y and ε_x are fixed strains after cooling and load removal, and $\varepsilon_{x,rec}$ is the strain after recovery.

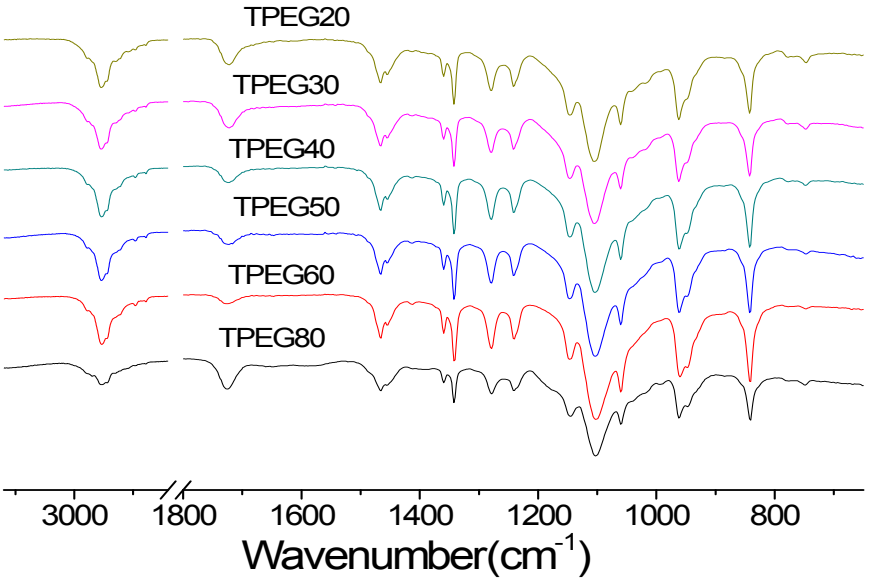


Figure S1. ATR-FTIR spectra of p(DMAEMA-co-TPEG) with different TPEG-content

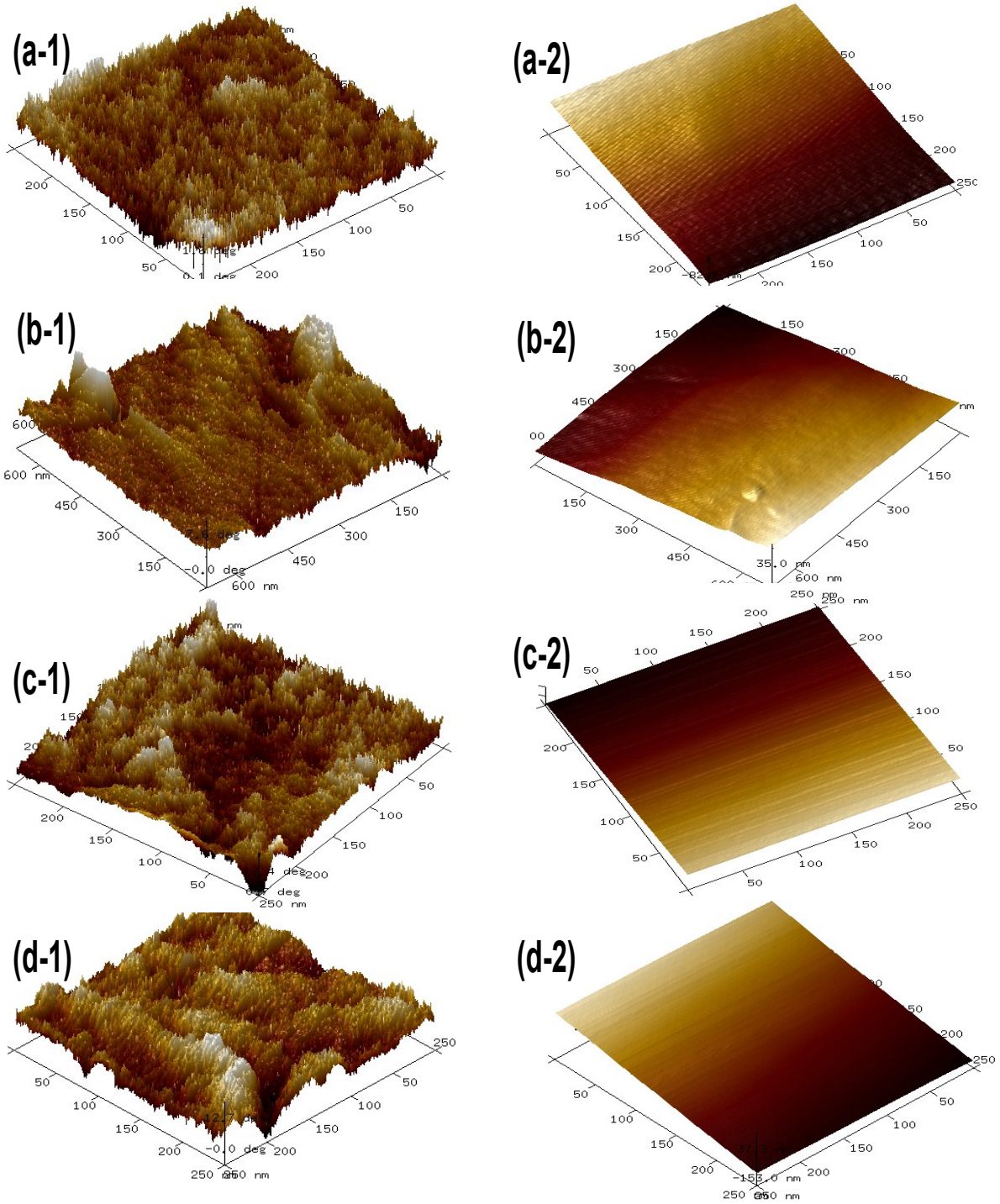
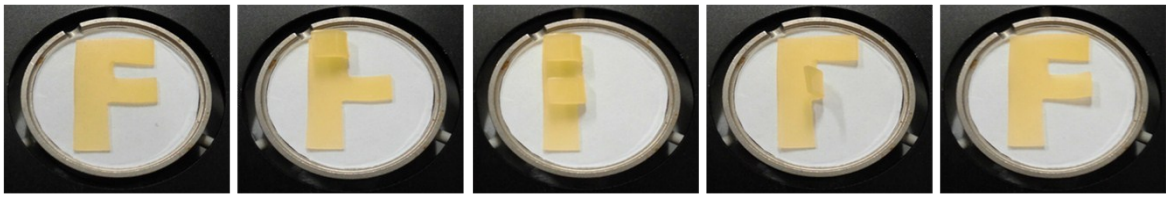


Figure S2.AFM 3D-images of p(DMAEMA-co-TPEG) with different TPEG-content：(a-TPEG20; b-TPEG50; c-TPEG60; d-TPEG80)



a b c d e

Figure S3. Pictures showing the triple-shape memory and recovery (a-original shape; b-the first temporary shape fixed at 70℃; c-the second temporary fixed at 20℃; d-the first recovered shape recovered at 70℃; c-the second recovered shape recovered at 110℃)

Table S1. DSC results of p(DMAEMA-co-TPEG)

Samples	On the second heating		On the cooling	
	△H (J/g)	Tm (℃)	ΔH (J/g)	T (℃)
TPEG	183.7	55.45	172.7	29.43
TPEG80	124.5	52.53	124.8	24.80
TPEG60	97.30	52.86	84043	24.08
TPEG50	59.04	52.56	37.12 | 9.63*	22.51 | -18.12&
TPEG40	59.63	54.40	34.75 | 6.28*	24.59 | -18.12&
TPEG30	45.37	49.43	16.23	-20.65
TPEG20	36.61	49.38	20.11	-19.09

Temperature (&) and enthalpy (*) from the second crystallisation peak on cooling

Table S2. Parameters for isothermal crystallization kinetics at 30°C

Sample	n	logK	K	E(J/mol)	t(0.5)/min	$K=\ln 2/[t(0.5)]^n$	logK(t(0.5))
TPEG	1.53	-0.18	0.67	177.12	1.05	0.64	-0.19
TPEG80	1.72	-0.43	0.37	130.69	1.44	0.37	-0.43
TPEG60	2.33	-1.13	0.08	67.67	2.62	0.07	-1.13
TPEG50	2.33	-1.67	0.02	47.90	4.51	0.02	-1.68
TPEG40	1.98	-1.65	0.02	22.54	5.64	0.02	-1.64