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Development of Zwitterionic Polyurethanes with Multi-Shape Memory Effects and Self-healing Properties

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Supporting Information

Test 1: Shape Memory Behavior Testing

The temperature-induced shape-memory behaviors were determined with cyclic thermo-mechanical analysis in accordance with. 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 ca.T_g+20°C (based on DSC) 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. T_g-20°C with q=-10°C/min, followed by equilibration for 10min; (4) unloading external force 0N at a rate of 0.25N/min; (5) reheating to ca.T_g+20°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. T_g+40°C (based on DSC) 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 T_g with q=-10°C/min, followed by equilibration for 10min; (4) further fixing the strain by quickly cooling to T_g-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 T_g at a rate of 4°C/min and followed by equilibration for 40min; (7) reheating to ca. T_g+40°C at a rate of 4°C/min and followed by equilibration for 40min.

3) For quadruple-shape-memory cycles: (1) heating to T_g+60°C (based on DSC) 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 T_g+45°C with q=-10°C/min, followed by equilibration for 10min; (4) further fixing the strain by quickly cooling to T_g+30°C with q=-10°C/min, followed by equilibration for 10min; (5) further fixing the strain by quickly cooling to 0°C with q=-10°C/min, followed by equilibration for 10min; (6) unloading external force 0N at a rate of 0.25N/min; (7) reheating to T_g+30°C at a rate of 4°C/min and followed by equilibration for 40min. (8) further reheating to T_g+45°C at a rate of 4°C/min and followed by equilibration for 40min. (9) further reheating to T_g+60°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:

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

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

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

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

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

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.

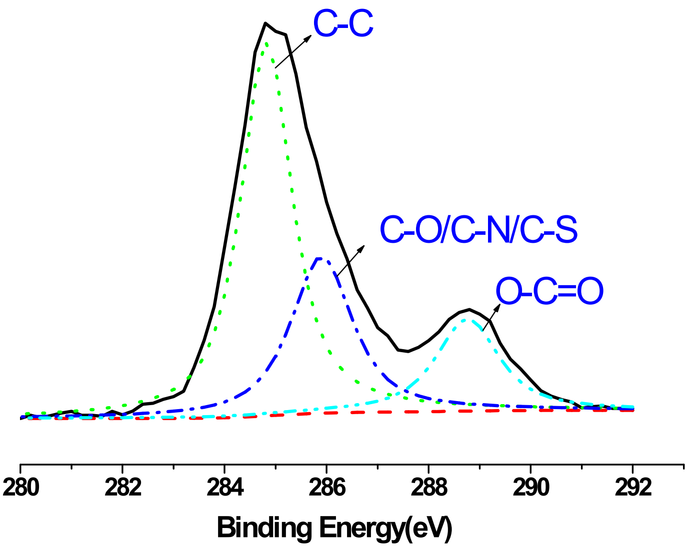


Figure S1. **XPS-C$_{1s}$ spectra of Zwitterionic shape memory polyurethane**

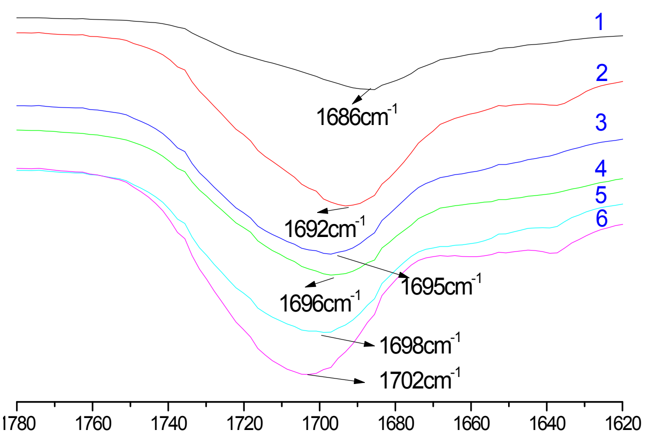


Figure S2. FT-IR Spectra in the region of C=O vibration of zwitterionic shape memory polyurethane with different MDEAPS content (1-ZSMPU0; 2-ZSMPU2; 3-ZSMPU4; 4-ZSMPU5; 5-ZSMPU6; 6-ZSMPU8)

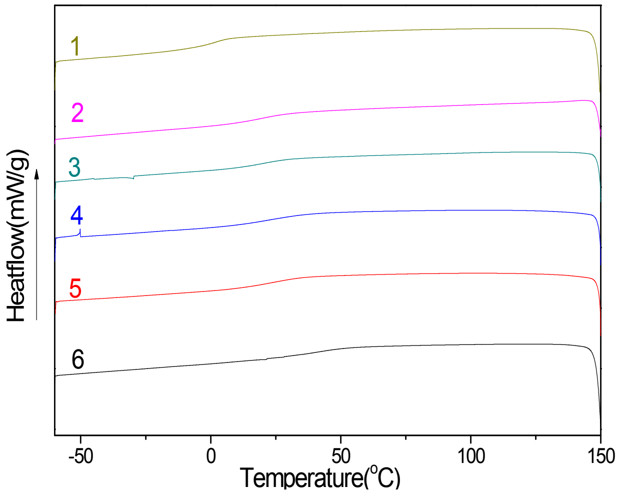


Figure S3. DSC cooling curves of zwitterionic shape memory polyurethane with different MDEAPS content (1-ZSMPU0; 2-ZSMPU2; 3-ZSMPU4; 4-ZSMPU5; 5-ZSMPU6; 6-ZSMPU8)

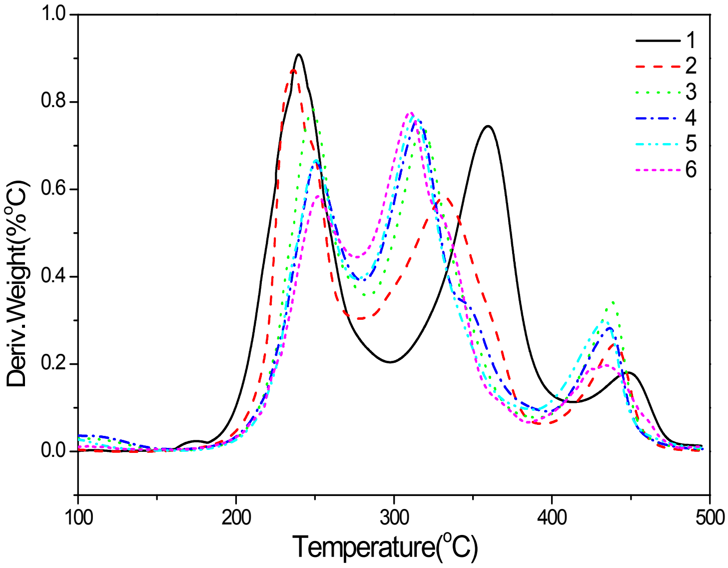


Figure S4. DTG curves of zwitterionic shape memory polyurethane with different MDEAPS content (1-ZSMPU0; 2-ZSMPU2; 3-ZSMPU4; 4-ZSMPU5; 5-ZSMPU6; 6-ZSMPU8)

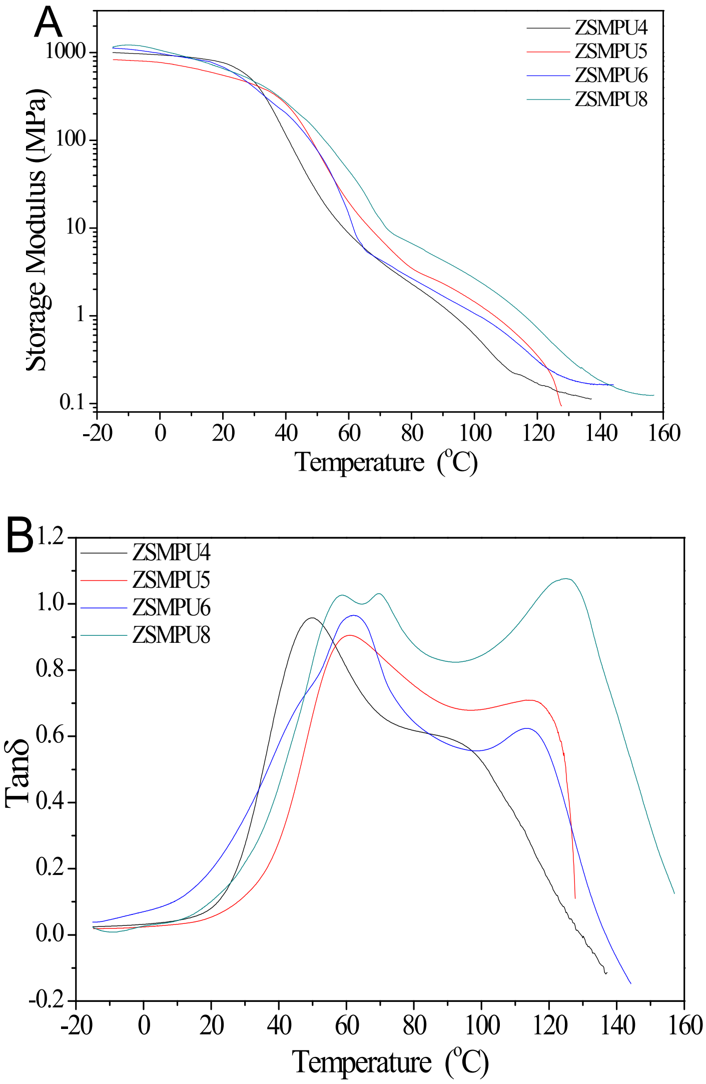


Figure S 5. DMA curves (A)E'(T); b) tanδ(T)) of zwitterionic shape memory polyurethanes determined under 10 Hz and a heating rate of 1.0 K/min

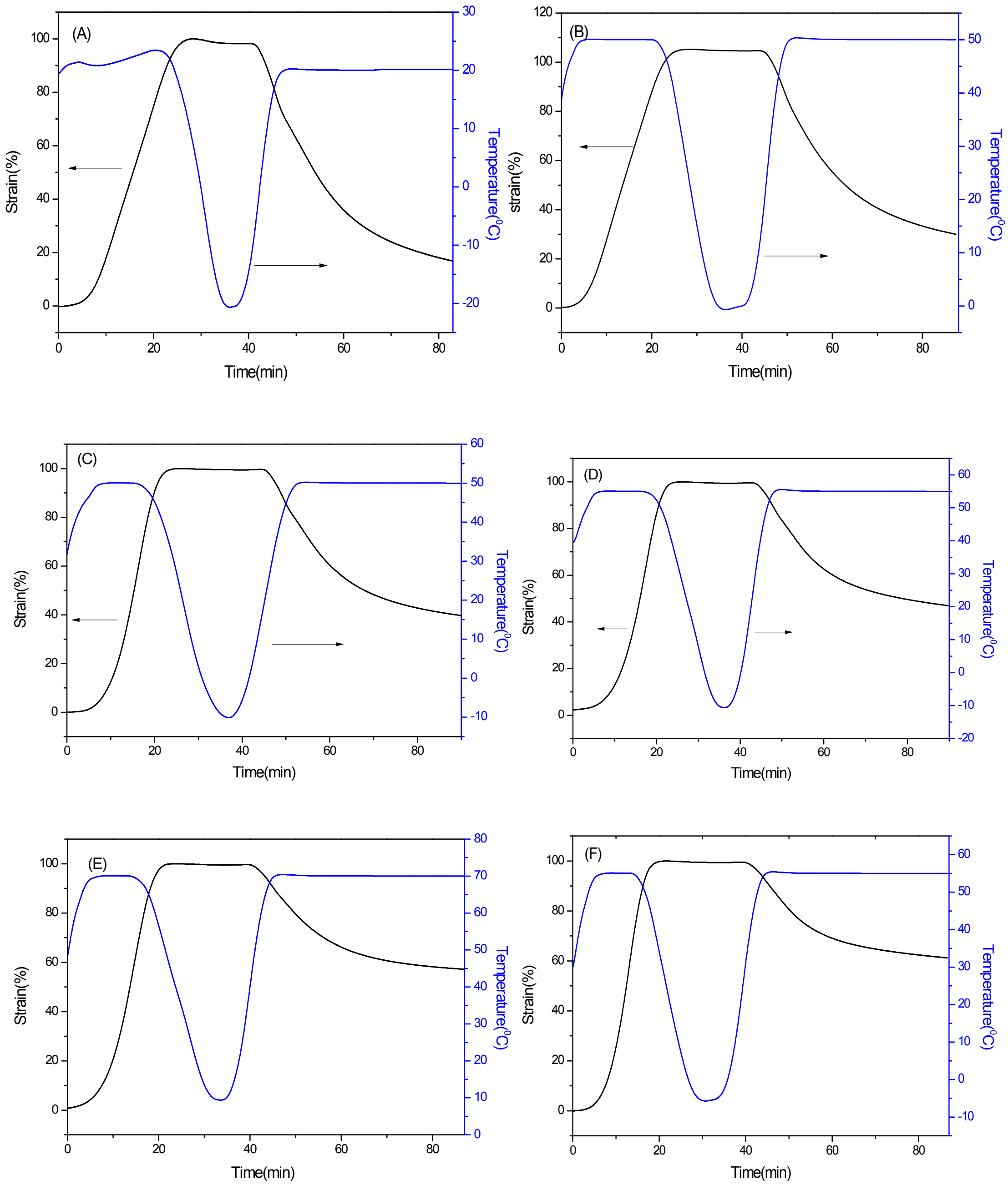
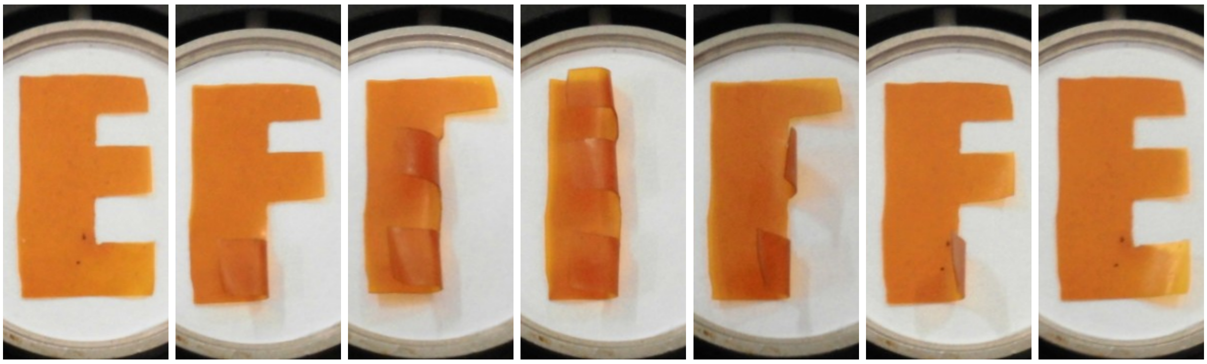


Figure S6 Dual-shape memory behaviors of ZSMPU with different MDEAPS content (A-ZSMPU0; B-ZSMPU2; C-ZSMPU4; D-ZSMPU5; E-ZSMPU6; F-ZSMPU8)



(a) (b) (c) (d) (e) (f) (g)

Figure S7. photos showing the quadruple-shape-memory behaviours of ZSMPU4 (a-original shape; b-the fixed temporary shape 1 at 73℃ after the first deformation at 88℃; c--the fixed temporary shape 2 at 58℃ after the second deformation at 73℃; d--the fixed temporary shape 3 at 0℃ after the third deformation at 58℃; e-the recovering shape at 58℃ on the first shape recovery; f--the recovering shape at 73℃ on the second shape recovery; g--the recovering shape at 88℃ on the third shape recovery)

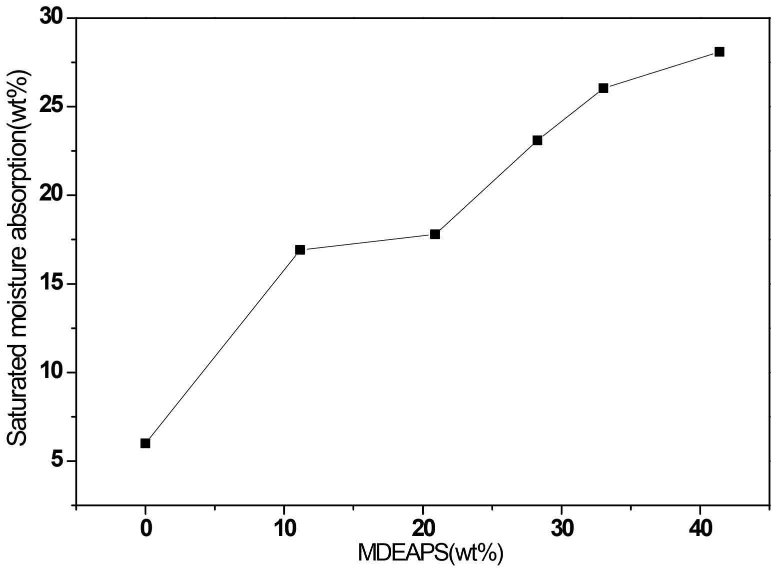


Figure S8 Dependency of Saturated moisture absorption on MEDAPS content

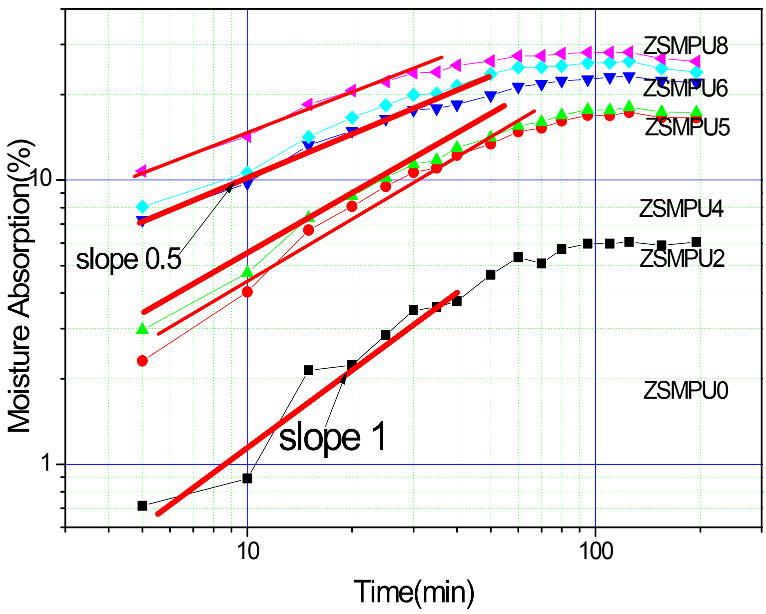


Figure S9 Log-Log plot showing the Moisture absorption of ZSMPU with different MDEAPS content

Table S1. Strain fixity and strain recovery in each step for triple-shape memory effect of ZSMPUs

Samples	Strain fixity 1(%)	Strain fixity 2(%)	Strain Recovery 1(%)	Strain Recovery 2(%)	Total strain recovery (%)
ZSMPU2	48.88	98.05	101.0	89.68	97.50
ZSMPU4	72.08	98.80	101.80	72.08	91.20
ZSMPU5	85.72	99.30	87.00	72.85	81.91

Strain fixity 1: Strain fixity on first step; Strain fixity 2: Strain fixity on second step; Strain Recovery 1: Strain recovery on first step; Strain Recovery 2: Strain recovery on second step;