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 ($\varepsilon_{\text{load}}$) by ramping force from 0.001N to 1N at a rate of 0.25N/min; equilibration for 3 min; (3) fixing the strain ($\varepsilon$ ) 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 ($\varepsilon_{\text{rec}}$ ) 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:

$$R_f=100\%\times\varepsilon/\varepsilon_{\text{load}}$$

(1)
\[ R_{r} = 100\% \times \frac{(\varepsilon - \varepsilon_{\text{rec}})}{\varepsilon} \quad (2) \]

Where \( \varepsilon_{\text{load}} \) represents the maximum strain under load, \( \varepsilon \) is the fixed strain after cooling and load removal, and \( \varepsilon_{\text{rec}} \) is the strain after recovery.

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

\[ R_{f}(X \rightarrow Y) = 100\% \times \frac{(\varepsilon_{y} - \varepsilon_{x})}{(\varepsilon_{\text{load}} - \varepsilon_{x})} \quad (3) \]

\[ R_{f}(Y \rightarrow X) = 100\% \times \frac{(\varepsilon_{y} - \varepsilon_{x,\text{rec}})}{(\varepsilon_{y} - \varepsilon_{x})} \quad (4) \]

Where \( X \) and \( Y \) denote two different shapes, respectively, \( \varepsilon_{\text{load}} \) represents the maximum strain under load, \( \varepsilon_{y} \) and \( \varepsilon_{x} \) are fixed strains after cooling and load removal, and \( \varepsilon_{x,\text{rec}} \) is the strain after recovery.
Figure S1. XPS-C\textsubscript{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 S 5. DMA curves (A) $E'(T)$; b) $\tan\delta(T)$ 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)
Figure S7. photos showing the quadruple-shape-memory behaviours of ZSMPU4 (a-original shape; b-the fixed temporary shape 1 at 73°C after the first deformation at 88°C; c--the fixed temporary shape 2 at 58°C after the second deformation at 73°C; d--the fixed temporary shape 3 at 0°C after the third deformation at 58°C; e-the recovering shape at 58°C on the first shape recovery; f--the recovering shape at 73°C on the second shape recovery; g--the recovering shape at 88°C 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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Strain fixity 1(%)</th>
<th>Strain fixity 2(%)</th>
<th>Strain Recovery 1(%)</th>
<th>Strain Recovery 2(%)</th>
<th>Total strain recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSMPU2</td>
<td>48.88</td>
<td>98.05</td>
<td>101.0</td>
<td>89.68</td>
<td>97.50</td>
</tr>
<tr>
<td>ZSMPU4</td>
<td>72.08</td>
<td>98.80</td>
<td>101.80</td>
<td>72.08</td>
<td>91.20</td>
</tr>
<tr>
<td>ZSMPU5</td>
<td>85.72</td>
<td>99.30</td>
<td>87.00</td>
<td>72.85</td>
<td>81.91</td>
</tr>
</tbody>
</table>

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;