Pyridine type zwitterionic polyurethane with both multi-shape memory effect and moisture-sensitive shape memory effect for smart biomedical application

Shaojun Chen[1], Zhankui Mei[1], Huanhuan Ren[1], Haitao Zhuo[2*], Jianhong Liu[2], Zaochuan Ge[1]

[1]Guangdong Research Center for Interfacial Engineering of Functional Materials; Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China; [2]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: H.T.Zhuo, haitaozhuo@163.com;

Supporting information

SI-1. Multi-Shape-Memory Behaviors Testing

The thermal-induced multi-shape-memory behaviors were determined with thermo-mechanical analysis using a TA Instruments DMA Q800 (using tension clamps in controlled force mode) according the procedure described in literatures.[4] All samples were dried at 100 °C in vacuum for 24 h and cut in rectangular pieces of approximately 8 mm × 2.0 mm × 0.3 mm. The detail test setup for dual-shape-memory cycles, triple-shape-memory cycles and quadruple-shape-memory cycles are provided below.[6]

a) For dual-shape-memory cycles: (1) heating to ca. 100°C followed by equilibration for 10 min; (2) uniaxial stretching to strain (ε_{load} =100%) at a rate of 0.1N/min; equilibration for 1 min; (3) fixing the strain (ε_f) by rapid cooling to 0°C with q=-10 °C/min, followed by equilibration for 10min; (4) unloading external force; (5) reheating to 100 °C at a rate of 10°C/min and followed by equilibration for 60min; the recovery strain (ε_{rec}) is finally recorded.

b) For triple-shape-memory cycles: (1) heating to T_g+40 °C and equilibrated for 10 min; (2) uniaxial stretching to strain (ε_{load1} =40%) at a rate of 0.1N/min; equilibration for 1 min; (3) fixing the strain by rapid cooling to T_g+20 °C with q=-10 °C/min, followed by equilibration for 10min;(4) uniaxial stretching to a second strain (ε_{load2} =100%) at a rate of 0.1N/min;, followed by equilibration for 1min; (5) further fixing the strain by rapid cooling to 0 °C with q=-10 °C/min, followed by equilibration for 10min; (6) unloading external force at a rate of 0.15 N/min, followed by equilibration for 10min; (7) reheating to T_g+20 °C at a rate of 10 °C/min and followed by equilibration for 40 min; (8) reheating to T_g+40 °C at a rate of 10 °C/min and followed by equilibration for 40 min.

c) For quadruple-shape-memory cycles: (1) heating to 127°C and equilibrated for 10 min; (2) uniaxial stretching to strain (ε_{load1} =30%) at a rate of 0.1N/min; equilibration for 1 min; (3) fixing the strain by rapid cooling to 105°C with q=-10 °C/min, followed by equilibration for 10 min; (4) uniaxial stretching to a second strain (ε_{load2} =60%) at a rate of 0.1N/min; equilibration for 1 min; (5) fixing the strain by rapid cooling to 92 °C with q=-10 °C/min, followed by equilibration for 10 min; (6) uniaxial stretching to a third strain (ε_{load3} =100%) at a rate of 0.1N/min; equilibration for 1 min; (7) fixing the strain by rapid cooling to 0°C with q=-10

°C/min, followed by equilibration for 10 min; (8)unloading external force at a rate of 0.15 N/min, followed by equilibration for 10 min; (9) reheating to 92 °C at a rate of 10 °C/min and followed by equilibration for 40 min. (10) further reheating to 105 °C at a rate of 10 °C/min and followed by equilibration for 40 min. (11) further reheating to 127 °C at a rate of 10 °C/min and followed by equilibration for 40 min.

SI-2. Moisture-Sensitive Shape Memory Behaviors Testing

The moisture-sensitive shape memory behavior is trigged by moisture. The immersion time is the key parameter. Thus, strain recovery versus immersion time curve is used to characterize the moisture-sensitive shape recovery behavior.[19] The detail test setups are provided below. Before testing, the specimens with a thickness of 1.0mm, a width of 5.0mm, a length of 20.0 mm (L_0 = 20 mm) were dried in an 100℃ vacuum oven for 12 hours, The specimens were stretched to a certain maximum elongation (L_{max}) at finite temperature beyond T_{trans} , e.g. 80 ℃. After they were fixed at a low temperature (e.g. 20 ℃) to a deformed strain (L_f), the deformed specimen was conditioned at a constant RH (e.g. 80% RH) and a constant temperature (e.g. 37 ℃). The temperature and RH can be adjusted. The length at any time (L_t) was then recorded each 10 minutes under the constant moisture condition. Finally, similar to the calculation method of thermal-induced SMEs described in literature, the moisture-sensitive strain recovery at any time (R_t) was calculated with the equation EQ.1.

$$R_t = (L_f - L_t)/(L_{max} - L_0) \times 100\% \qquad \text{EQ.1.}$$

Hence, the curve of strain recovery (R_t) versus immersion time (t) was obtained and used for characterizing the moisture-sensitive SMEs. Three specimens were tested in parallel. When the three curves are very close to each other, the obtained curves were taken for further analysis in each sample.

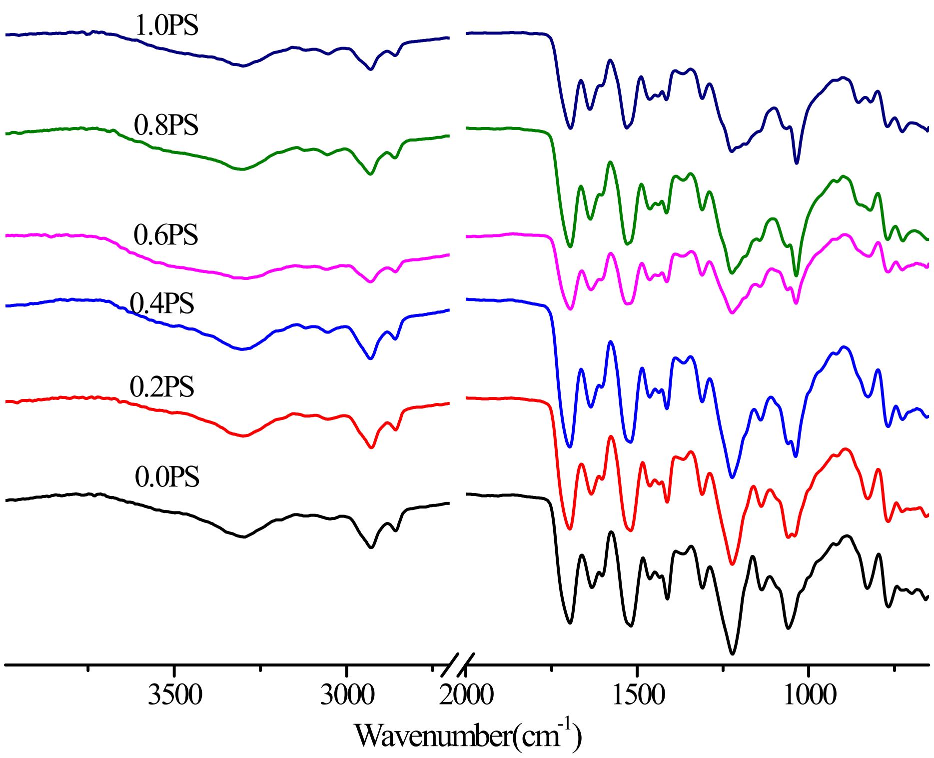


Figure S1. ATR-FTIR spectra of the pyridine type zwitterionic SMPUs with various PS/BINA ratios

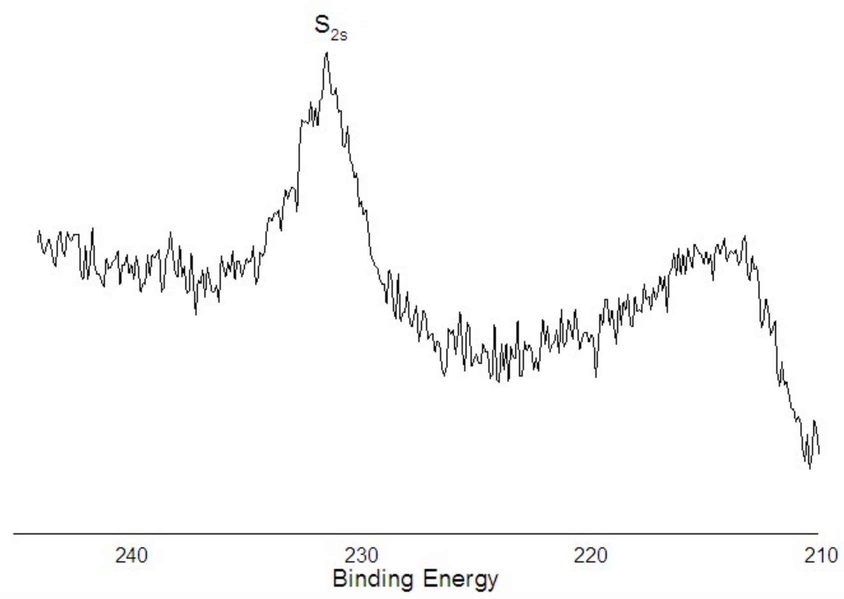


Figure S2. XPS survey of the sample PyZPU6 showing the existence of S_{2s} (binding energy, 230 eV)

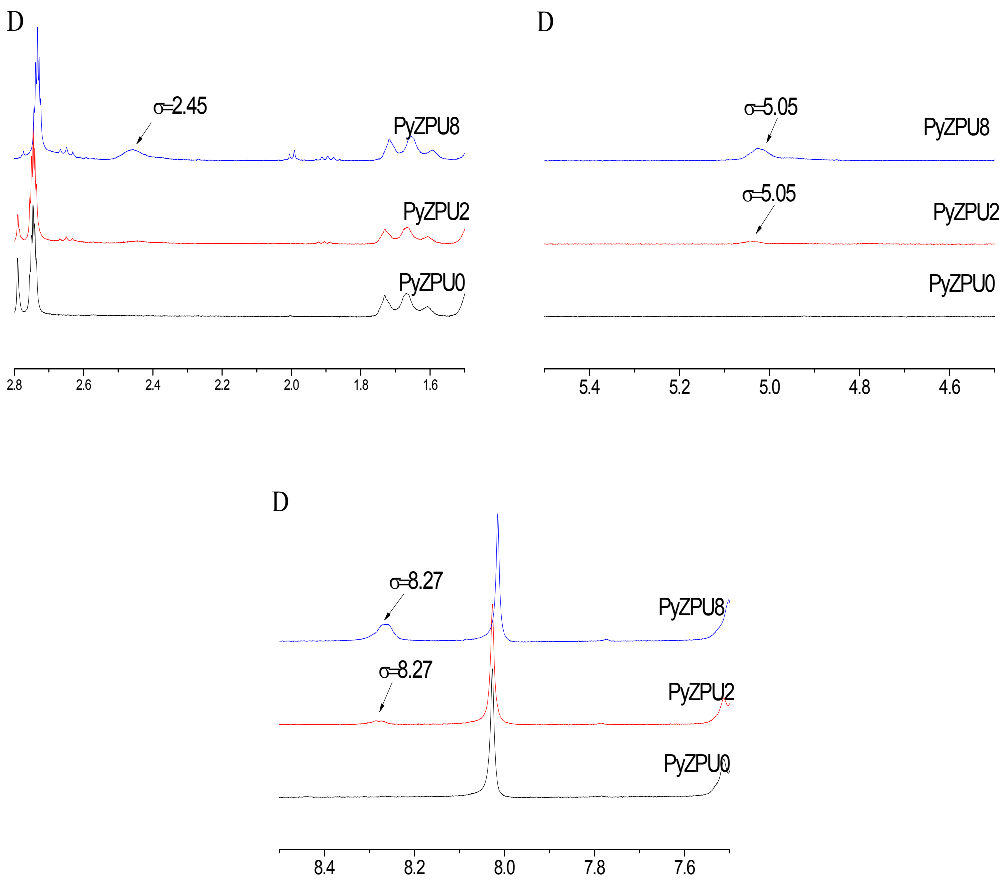


Figure S3. The Zoom peaks of pyridine zwitterionic segments at σ =2.45, 5.05, 8.27 in PyZPUs

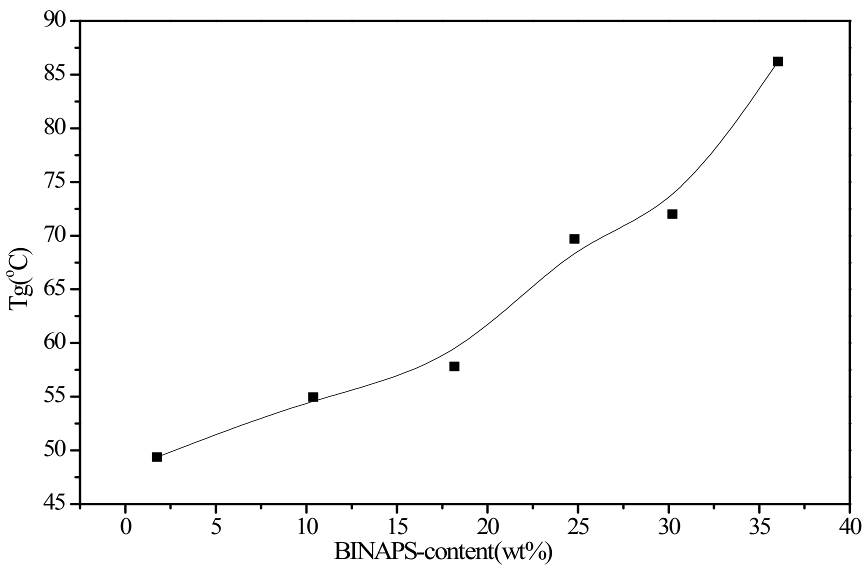


Figure S4 The dependency of T_g on the BINAPS content

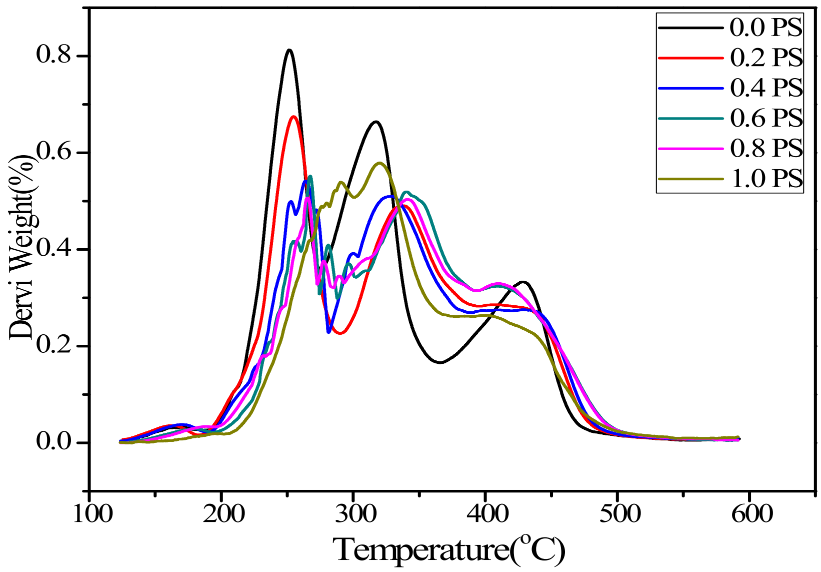


Figure S5. The DTG curves of the pyridine type zwitterionic SMPUs with various PS/BINA ratios

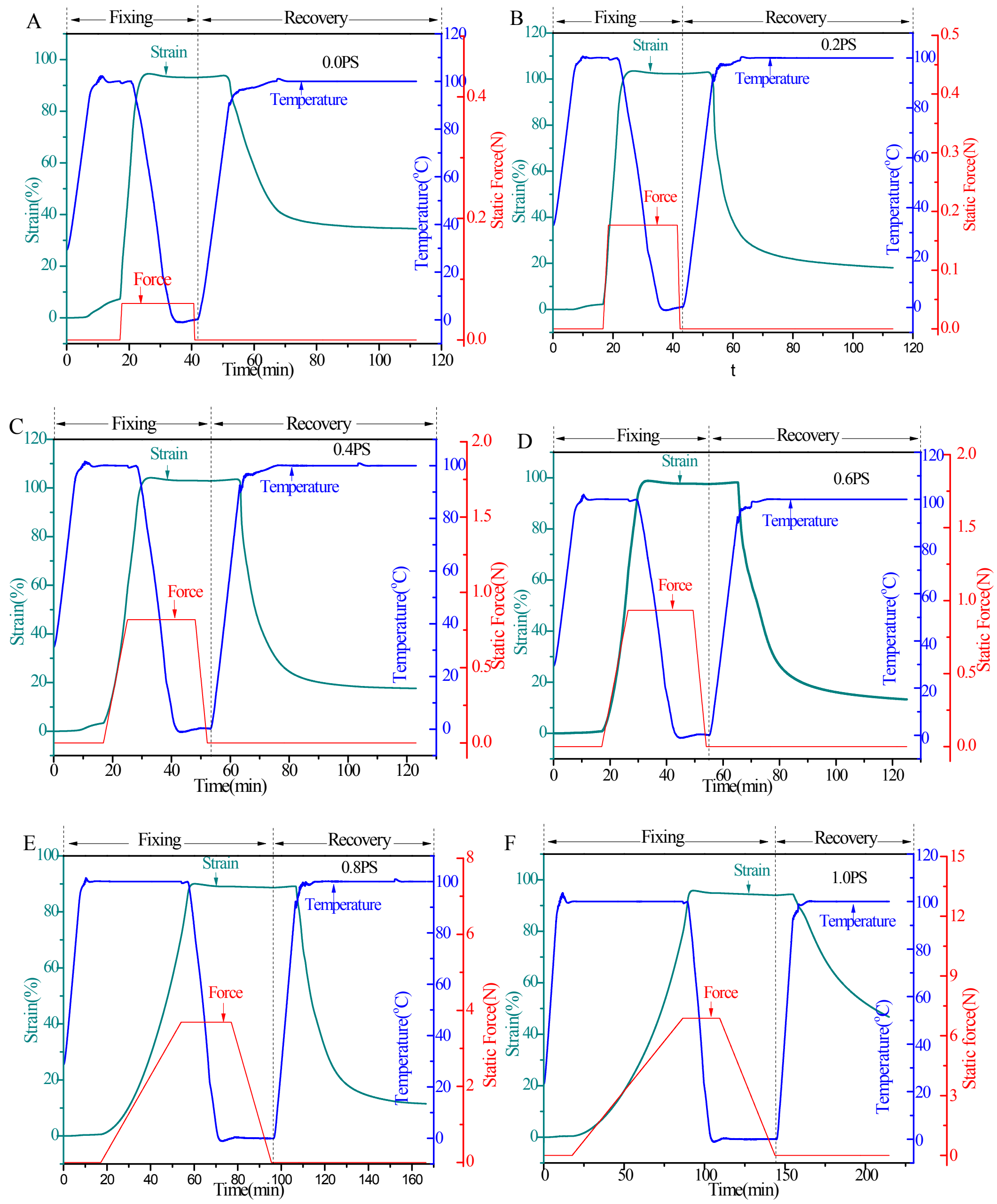


Figure S6. The dual-SMEs of PyZPUs with various PS/BINA ratios

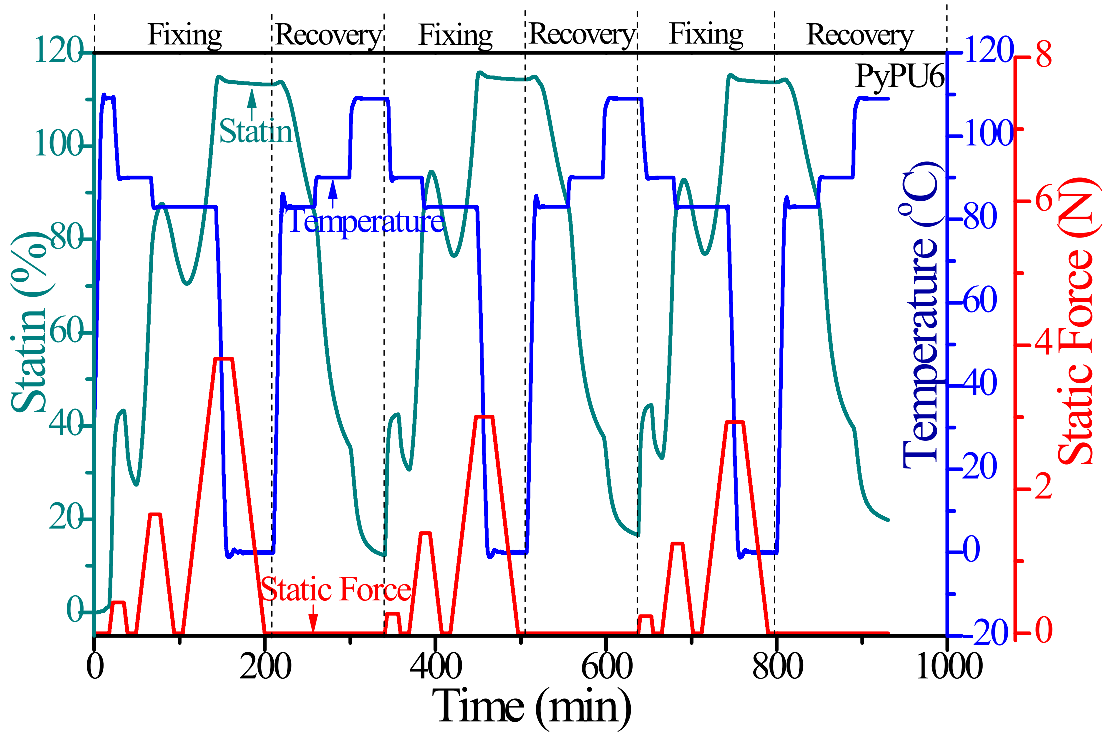


Figure S7 the repeatability of triple-SME of the PyZPUs

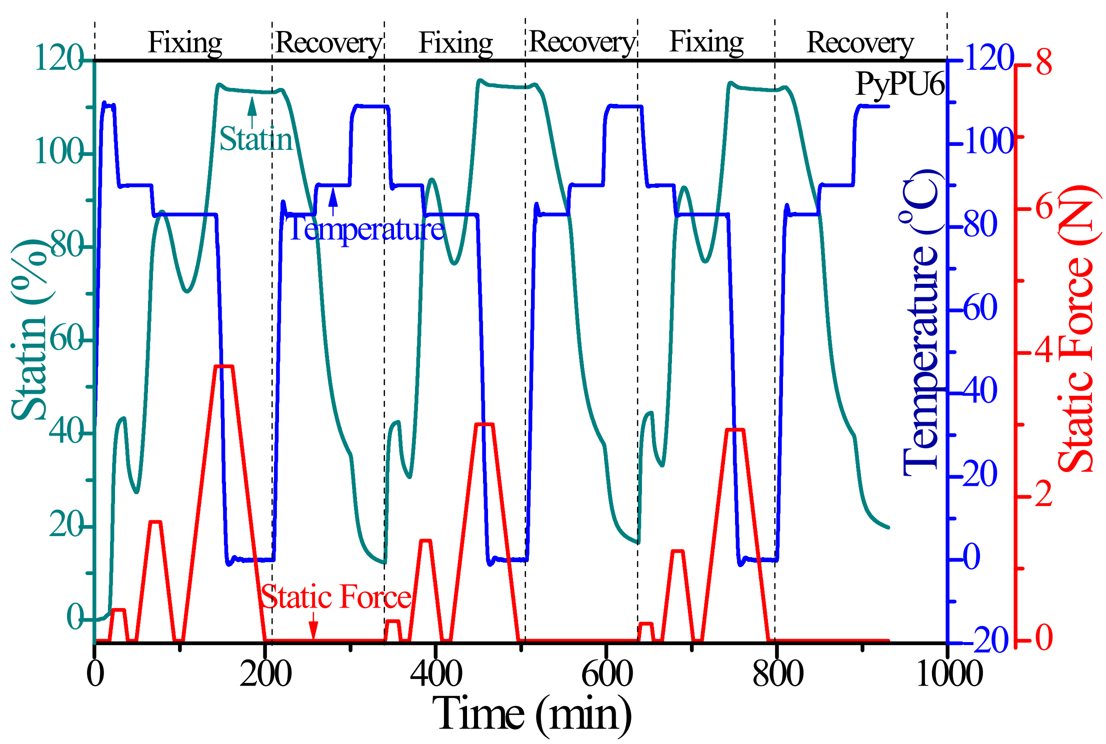
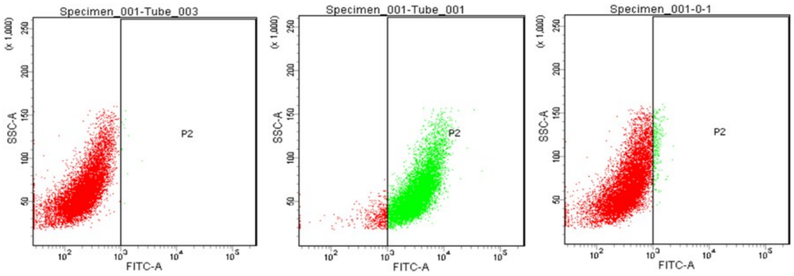
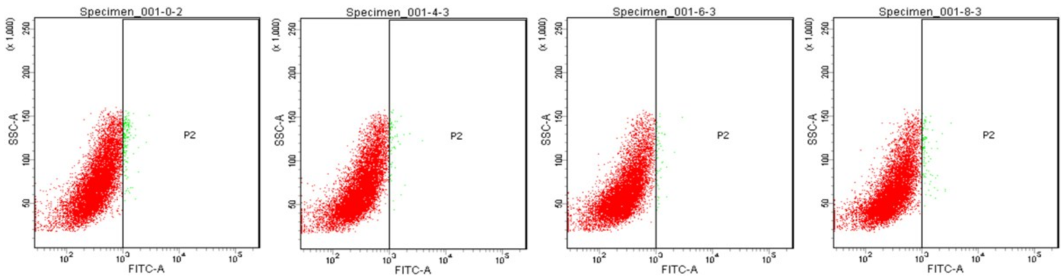


Figure S8. The repeatability of Qudruple-SME of the PyZPUs



(a) Control (b)L (c) 0PS



(d)0.2PS (e)0.4PS (f)0.6PS (g)0.8PS

Figure S9. Dotplot of SSC-A/FITC-A for control, LPS, and PyZPUs with different PS/BINA ratio