

Supporting Information

Article

Recyclable shape-memory waterborne polyurethane films based on perylene bisimide modified polycaprolactone diol

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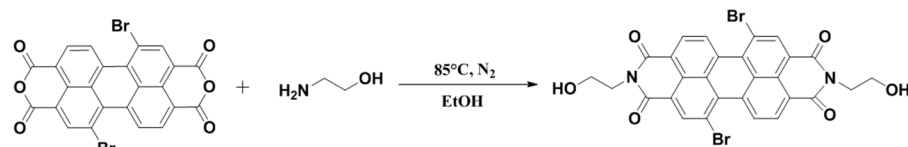
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1. Experimental Section

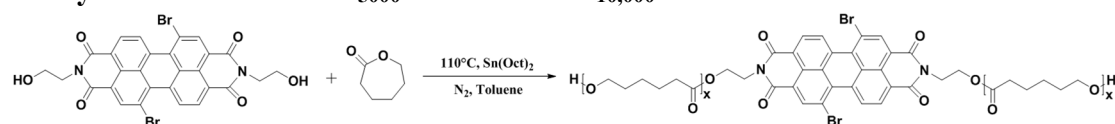
1.1 Synthesis of PBI-OH



Scheme S1 Synthesis of PBI-OH.

1,7-dibromo-3,4,9,10-per tetracarboxylic dianhydride (1 g, 1.82 mmol), ethanolamine (0.334 g, 5.46 mmol) and absolute ethanol (15 ml) were placed in a three-necked flask equipped with a magnet stirrer under nitrogen atmosphere at 85°C for 5 h. After the reaction, the mixture was cooled to room temperature and diluted with ethanol (50 ml). The precipitate was obtained through centrifugation and purified with cooled ethanol (4×20 ml). Finally, the products were dried for 24 h at 60°C in vacuum and 0.9807 g of product was obtained with yield of 86%. ¹H-NMR (400 MHz, CDCl₃): δ=9.59 (2H, d, phenyl-H), 8.98 (2H, s, phenyl-H), 8.78 (2H, d, phenyl-H), 4.60 (4H, s, -CH₂-), 4.22 (4H, s, -CH₂-).

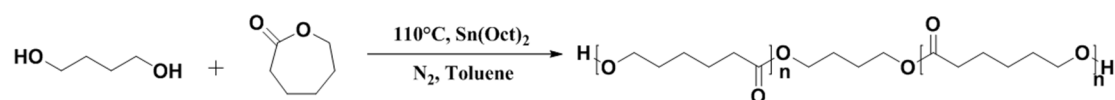
1.2 Synthesis of PBI-PCL₅₀₀₀ and PBI-PCL_{10,000}



Scheme S2 Synthesis of PBI-PCL₅₀₀₀ and PBI-PCL_{10,000}.

The PBI-PCL (PBI-PCL₅₀₀₀ and PBI-PCL_{10,000}, where the number indicates the molecular weight of poly(ε-caprolactone) (PCL)) were synthesized from PBI-OH and ε-CL through controlling the content of ε-CL. PBI-PCL₅₀₀₀ was chosen as an example. In a typical reaction, PBI-OH (2 g, 3.14 mmol), ε-CL (14.35 g, 125.74 mmol), Sn(Oct)₂ (0.1435g, as catalyst) and anhydrous toluene (30 ml) were mixed into a three-necked round bottom flask. The mixture was vigorously stirred at room temperature for 5 min and then stirred at 110°C for another 20 h under dry nitrogen. After that, After the reaction, the mixture was cooled to room temperature and diluted with ethanol (150 ml). The precipitate was obtained through centrifugation and purified with cooled methanol (4×30 ml). The product was obtained after drying in vacuum oven at 40°C for 24 h and 15.12 g of product was obtained with yield of 89%. ¹H-NMR (400 MHz, CDCl₃) δ=9.51 (2H, d, phenyl-H), 8.93 (2H, d, phenyl-H), 8.71 (2H, s, phenyl-H), 4.48 (4H, s, -CH₂-), 4.24 (4H, s, -CH₂-), 4.06 (84H, t, -CH₂-), 3.65 (4H, t, -CH₂-OH), 2.31 (84H, t, -CO-CH₂-), 1.65 (168H, m, -CH₂), 1.38 (84H, t, -CH₂). PBI-PCL_{10,000} was prepared in the same manner.

1.3 Synthesis of BDO-PCL₅₀₀₀ and BDO-PCL_{10,000}



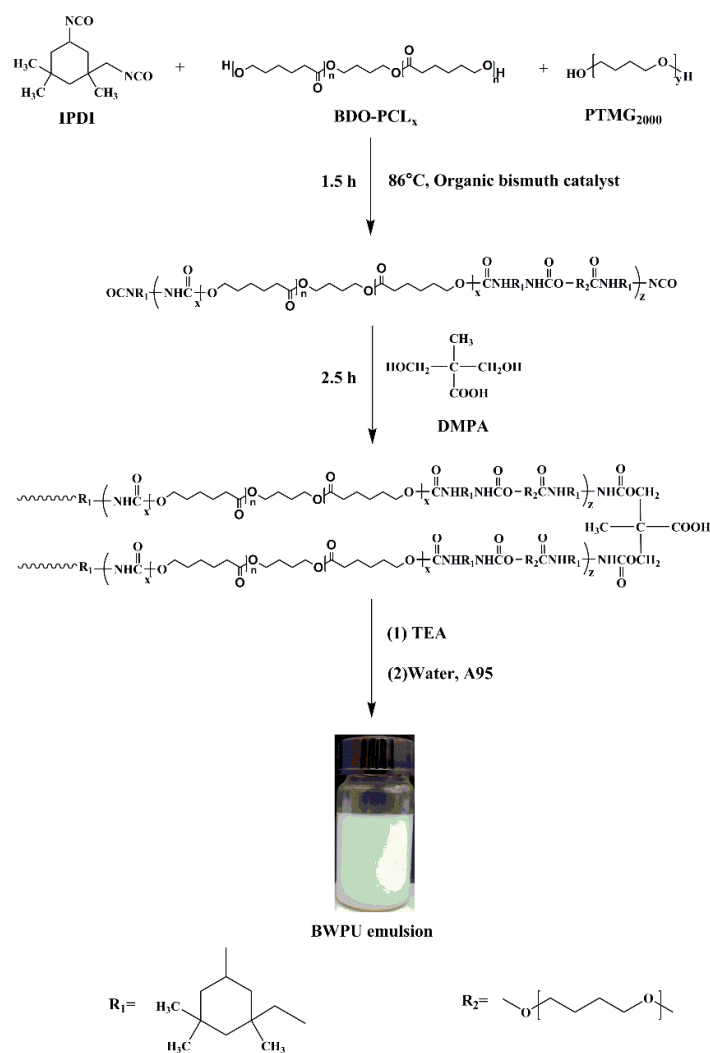
Scheme S3 Synthesis of BDO-PCL₅₀₀₀ and BDO-PCL_{10,000}.

BDO-PCL₅₀₀₀ and BDO-PCL_{10,000} was prepared in the same manner as PBI-PCL₅₀₀₀ and PBI-PCL_{10,000}.

1.4 Synthesis of PWPU₅₀₀₀, PWPU₁₀₀₀₀, BWPU₅₀₀₀ and BWPU_{10,000}

In a typical procedure of BWPU₅₀₀₀ and PWPU₅₀₀₀ (BWPU_{10,000}, BWPU₅₀₀₀ and PWPU_{10,000} where the number indicates the corresponding PCL used), PWPU₅₀₀₀ was chosen as an

example. In a typical reaction, PBI-PCL₅₀₀₀ (4 g, 0.8 mmol), PTMG₂₀₀₀ (38.4 g, 19.2 mmol) and IPDI (13.32 g, 60 mmol) were added into a dry three-neck flask equipped with a mechanical stirrer, 0.05 ml of organobismuth catalyst was added and stirred in an oil bath at 86°C for 1.5 h. After DMPA (2.76 g, 20 mmol) was added and the reaction was continued for 2.5 h, an appropriate amount of acetone was added to the system to reduce its viscosity. When the reaction mixture was slowly cooled to 45°C, TEA (2.08 g, 20 mmol) was added to the system to neutralize the side chain carboxyl groups, and finally the polymer was added to 120 ml deionized water and the solution was emulsified by stirring at high shear speed, and finally A95 was added dropwise to post-expand the chain to obtain PWPU emulsion. PWPU_{10,000}, BWPU₅₀₀₀ and BWPU_{10,000} were obtained using PBI-PCL_{10,000}, BDO-PCL₅₀₀₀ and BDO-PCL_{10,000} in the same way.



Scheme S4 Synthesis of BWPU₅₀₀₀ and BWPU_{10,000}.

2. Additional Experimental Results

2.1 ^1H -NMR Spectra of PBI, PBI-PCL₅₀₀₀ and PBI-PCL_{10,000}

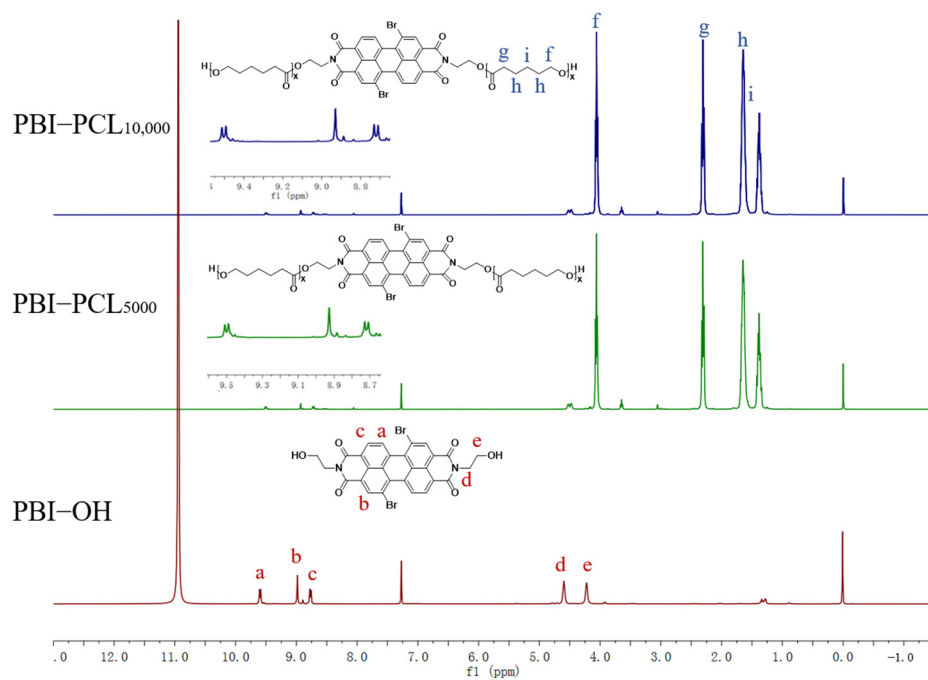


Figure S1 ^1H -NMR spectra of PBI, PBI-PCL₅₀₀₀ and PBI-PCL_{10,000}.

2.2 ^1H -NMR Spectra of BDO-PCL₅₀₀₀ and BDO-PCL_{10,000}

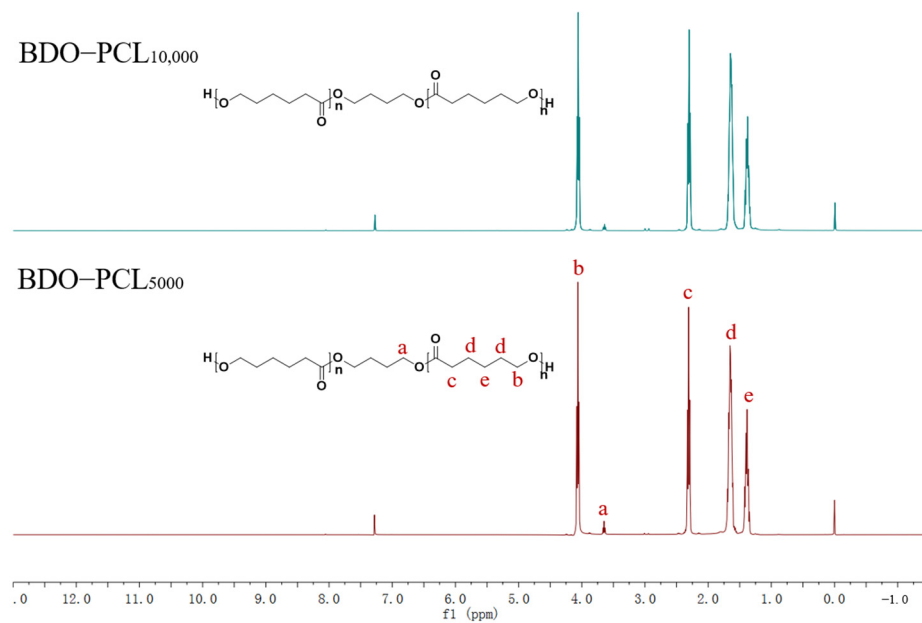


Figure S2 ^1H -NMR spectra of BDO-PCL₅₀₀₀ and BDO-PCL_{10,000}.

2.3 FTIR spectra of BDO, BDO-PCL_{10,000}, BWPU_{10,000} and PWPU_{10,000}

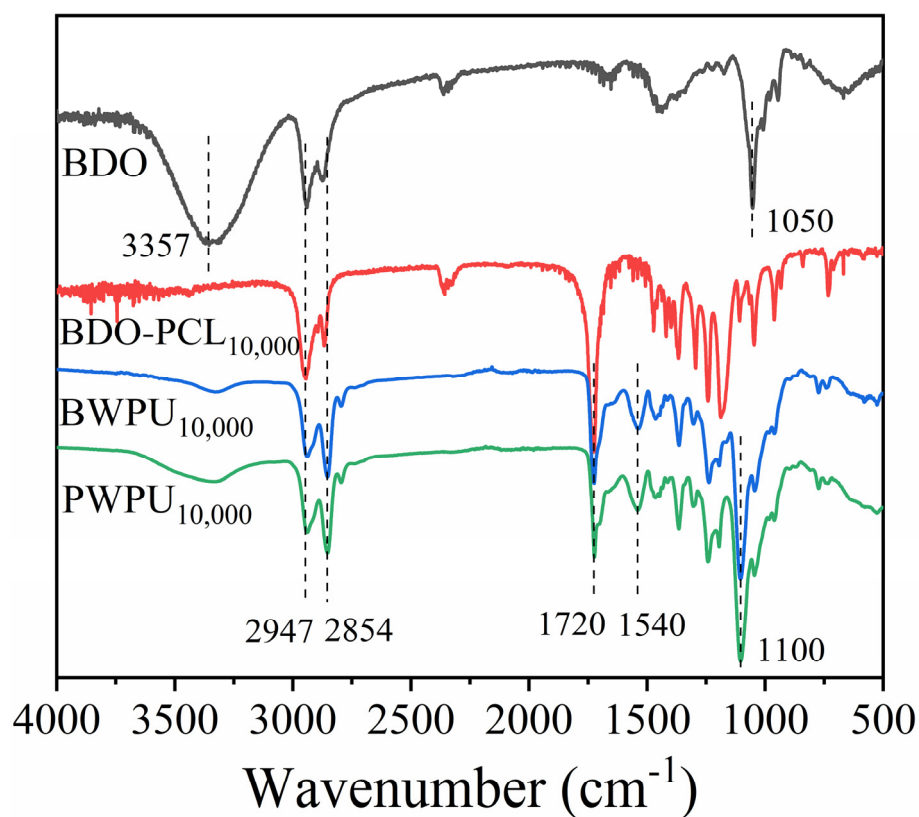


Figure S3. FTIR spectra of BDO, BDO-PCL_{10,000}, BWPU_{10,000} and PWPU_{10,000}.

2.4 The Zeta Potential Distribution of PWPU and BWPU Emulsions

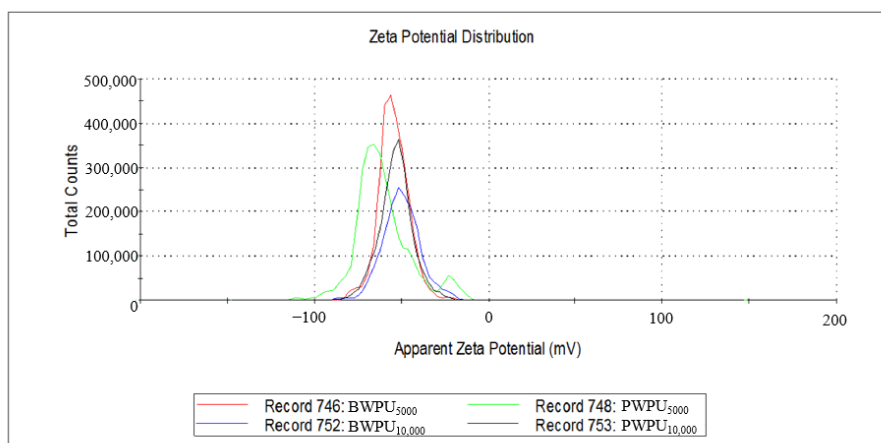


Figure S4 The zeta potential distribution of PWPU and BWPU emulsions.

3. Additional Experimental Results of Recyclable Performance Analysis

3.1 Screen the Recycled Solvent

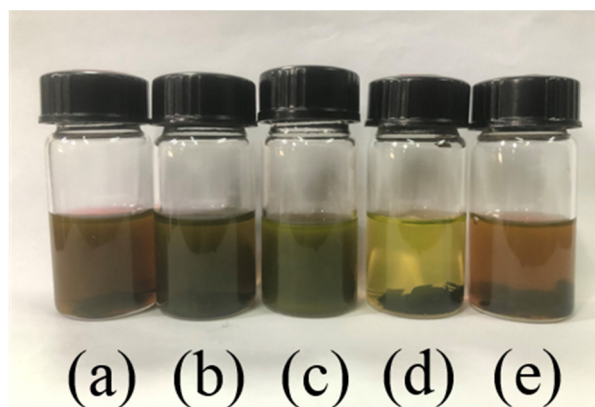


Figure S5 The dissolution images of PWPU_{10,000} under different solvents for 3 hours; (a)DMF; (b)NMP;(c) Acetone/Ethanol ($v/v = 2:1$) (d) Acetone; (e) Ethanol.

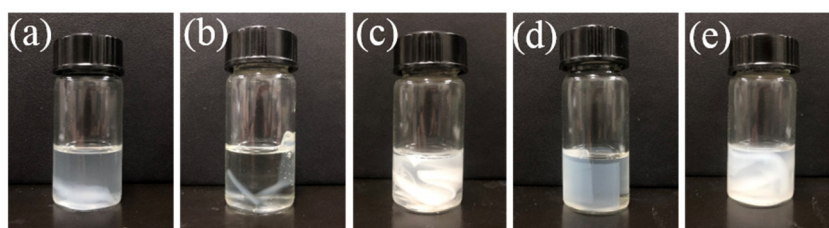


Figure S6 The dissolution images of BWPU_{10,000} under different solvents for 3 hours; (a)DMF; (b)NMP;(c) Acetone/Ethanol ($v/v=2:1$) (d) Acetone; (e) Ethanol.

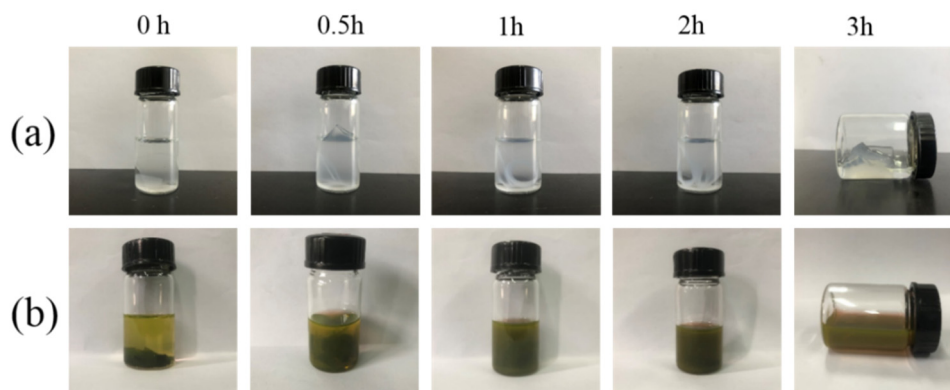


Figure S7 Photos of BWPU₅₀₀₀ (a) and PWPU₅₀₀₀ (b) with a mass of 0.5 g dissolved in 4 ml of acetone/ethanol mixed-solvent ($v/v=2:1$) at 25°C for 3 h.

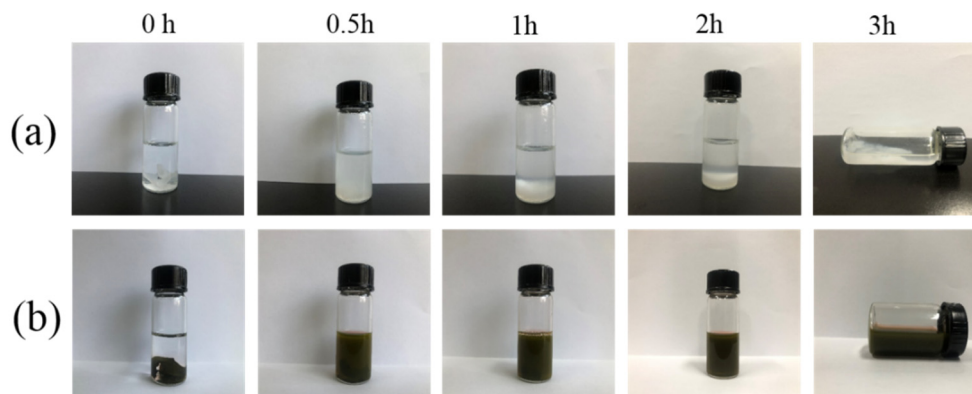


Figure S8 Photos of BWPU_{10,000} (a) and PWPU_{10,000} (b) with a mass of 0.5 g dissolved in 4 ml of acetone/ethanol mixed-solvent ($v/v=2:1$) at 25°C for 3 h.

3.2 The Zeta Potential Distribution of Recycled PWPU₅₀₀₀ and PWPU_{10,000} Emulsions

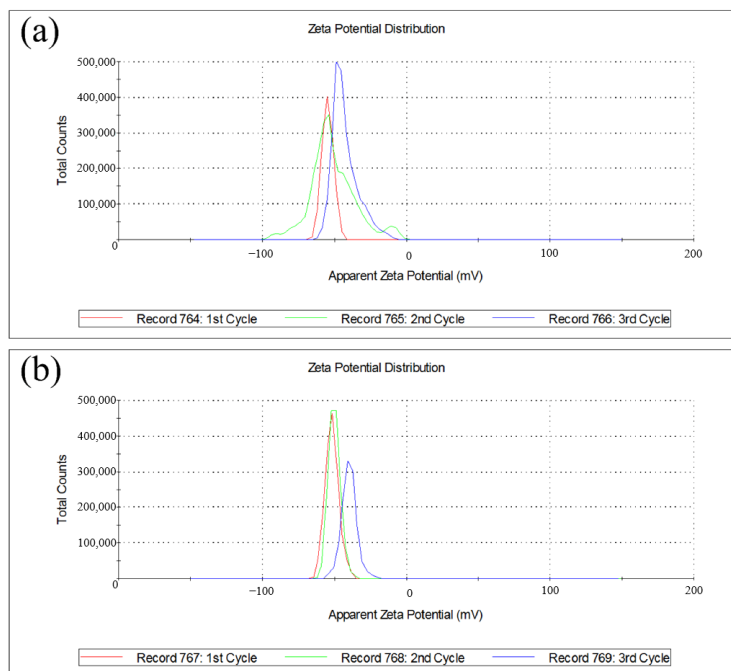


Figure S9 Zeta potential distribution of recycled PWPU₅₀₀₀ (a) and PWPU_{10,000} (b) emulsions.

3.3 Stress-strain Curves of Recycled PWPU₅₀₀₀ Film

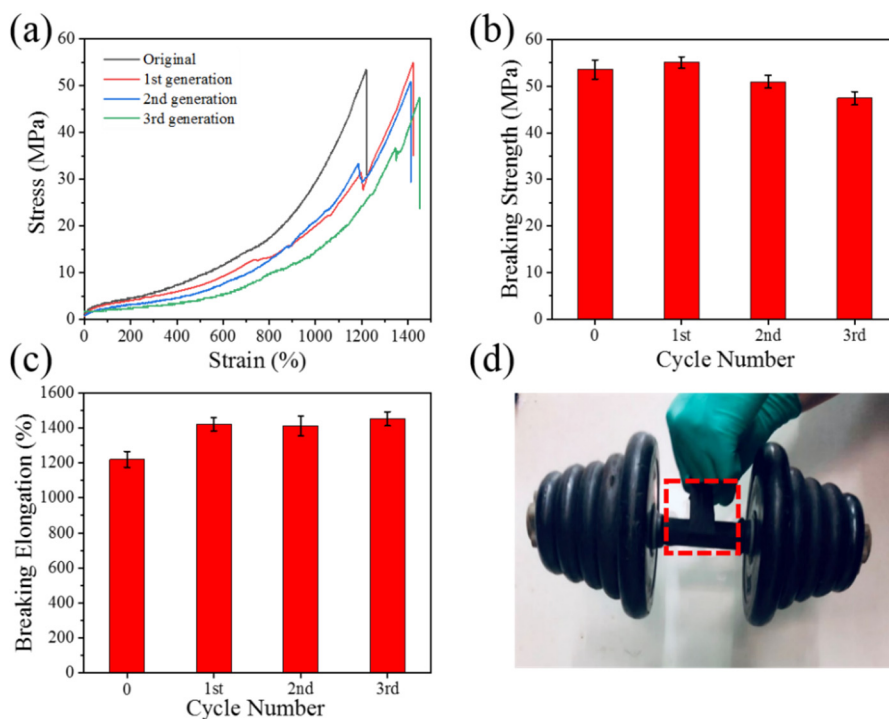


Figure S10 (a) Stress-strain curves of PWPU₅₀₀₀ after three-generations of recycling. The mechanical properties including the (b) breaking strength, and (c) breaking elongation for the PWPU₅₀₀₀ samples after three times recycling process. (d) Photo of lifting a 10 kg weight by a PWPU₅₀₀₀ film with the thickness of 0.3 mm after the recycling process.

4. Additional Experimental Results of Shape Memory

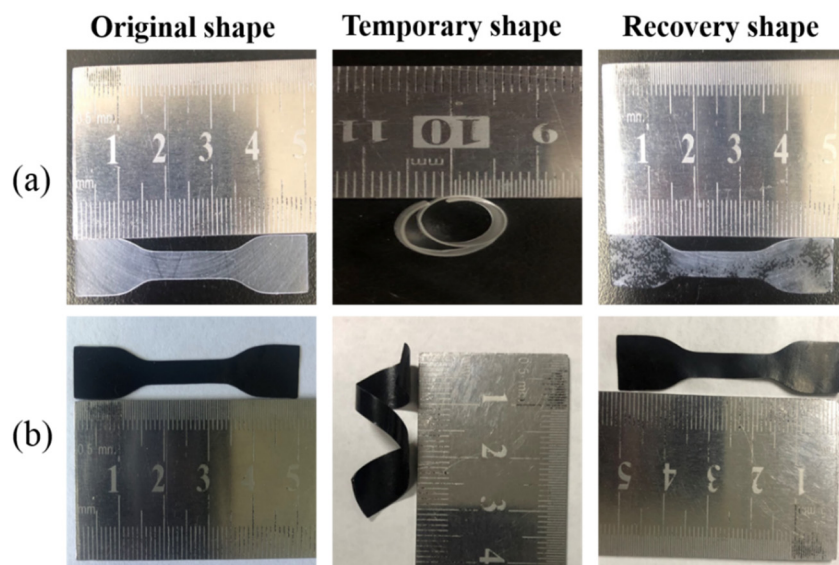


Figure S11 The shape memory behavior of BWPU_{10,000} (a) and PWPU_{10,000} (b) photos with original shape, temporary shape (deformed at 25°C for 20 min and fixed at 0°C for 20 min), and recovered state after being soaked in water at 70°C.

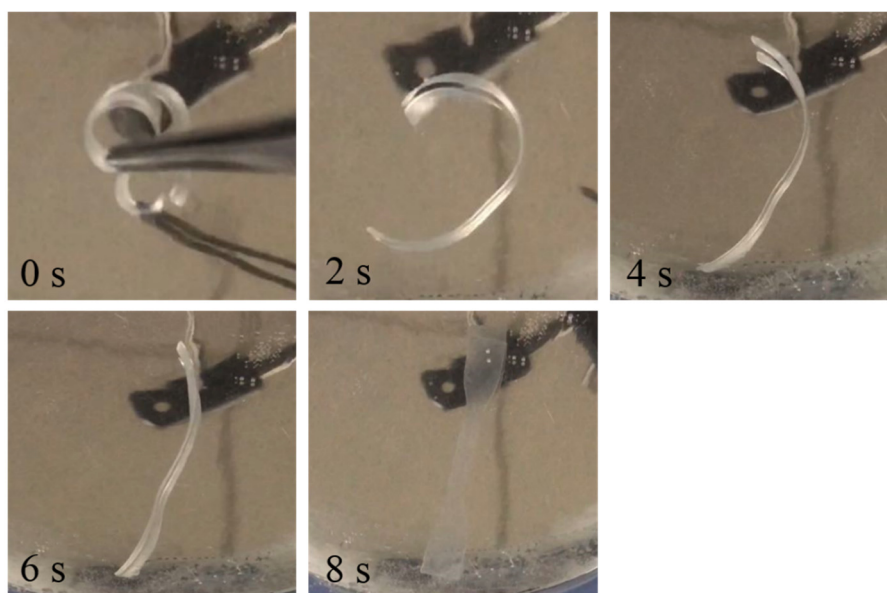


Figure S12 Photos of BWPU₅₀₀₀ shape recovery in water at 70°C.