Electronic supplementary information (ESI) for Light and Force Dual-Responsive Waterborne Polyurethane in Multiple States

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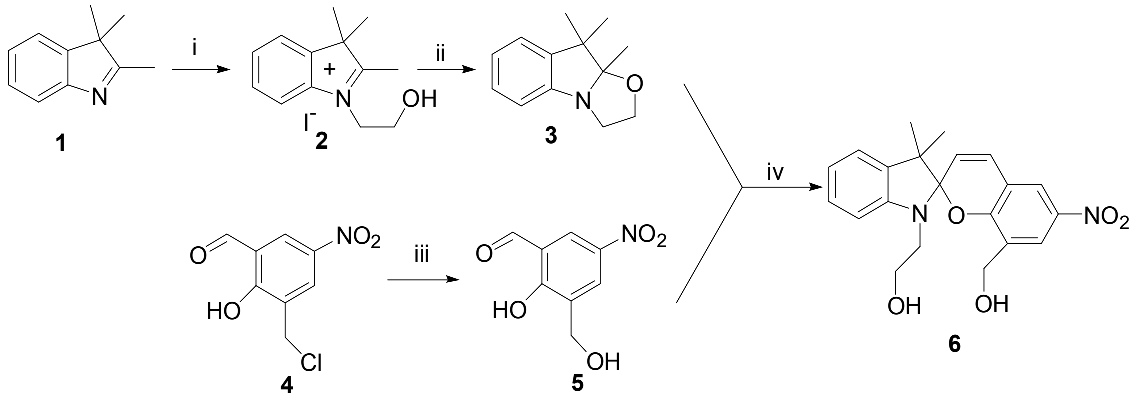
1. Synthesis of di-hydroxyl SP



Scheme S1. Synthesis of the di-hydroxyl SP

A mixture of 2,3,3-trimethlylindolenine (compound **1**, 9.62 g, 60.4 mmol) and 2-Iodoethanol (11.52 g, 67.0 mmol) was heated at 100℃ for 3.5h. A solid was obtained. It was dissolved in a mixture of water and ethyl acetate and then basified with sodium carbonate to PH 8. The Fisher base obtained was extracted with ether three times, dried over anhydrous sodium sulfate. The product was purified by silica gel chromatography (EtOAc: Hex =1:20). Yield: 65%.

3-Chloromethyl-5-nitrosalicylaldehyde (compound **4**, 5.742 g, 26.63 mmol) was dissolved in 30 mL of acetone and added to a 100 mL round bottom flask containing deionized water (10 ml) and a magnetic stir bar. The solution was heated to reflux with stirring for 20 min. Sodium hydroxide solution (4.45 ml of a 6 M solution) was added drop wise over a period of 10 minutes. The reaction mixture was stirred and refluxed for 3 h then cooled to room temperature. The resulting solution was filtered and chilled to precipitate the product. The material was recrystallized from water to obtain 3.913 g (yield: 60%) of light green crystals (compound **5**).

3-Hydroxymethyl-5-nitrosalicylaldehyde (compound **5**, 576 mg, 2.92 mmol) was dissolved in 10 mL of ethanol in a 50 ml round bottom flask. Water (10 ml) was added followed by addition of **3** (712 mg, 3.50 mmol). The reaction mixture was heated to reflux while stirring, and it was determined to be complete after a period of 5 h. The mixture was cooled to room temperature and then concentrated on a rotary evaporator to remove ethanol. Water (10 ml) was added and the mixture was brought to a boil. The solution was filtered and this procedure then repeated. The resulting brown powder was directly recrystallized from 70% acetonitrile (aq) solution to give dark golden crystals. ^{1}H NMR (400 MHz, acetone-d6) ∂: [8.22 & 8.04] (d, 2H, Ar-H), 7.17 (d, 1H, ArC*H* =CH-), 7.12 (m, 2 H, Ar-*H*), 6.81 (t, 1H, Ar-*H*), 6.69 (d, 1 H, Ar-*H*), 6.07 (d, 1H, -C*H*=CHAr), 4.43 (m, 2 H, ArCH_2OH), [3.80, 3.73, & 3.65] (m, 2 H, NCH$_2$CH_2OH), [3.40 & 3.31] (m, 2H, NCH_2CH$_2$OH), [1.27 & 1.18] (s, 3 H, C(CH_3)$_2$).

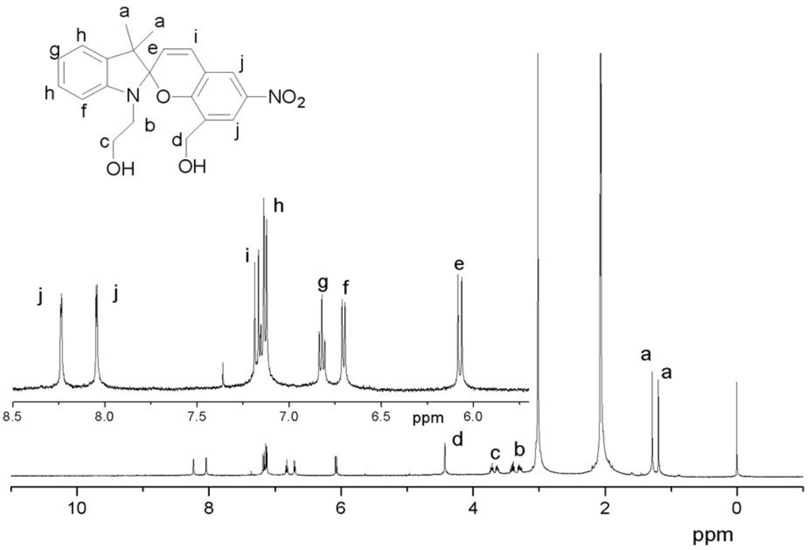


Figure S1. ^{1}H NMR of di-hydroxyl SP

2. Dynamic Light Scattering (DLS)

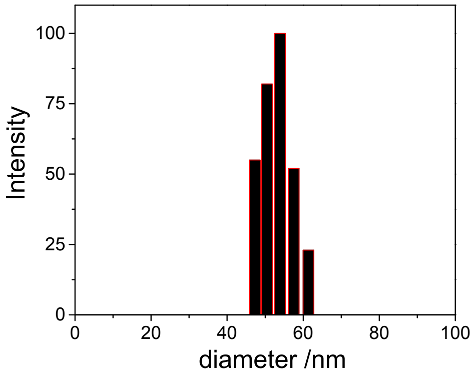


Figure S2. DLS of SP-WPU emulsion

DLS was test on a Brookhaven BI-200SM scattering meter, the concentration of SP-WPU emulsion was dilute to 10 mg/ml. Figure S3 showed that the diameter of the SP-WPU was 53 nm on average. Further analyze by AFM (Figure S3), it could be found that the average size of the polyurethane nanoparticles was around 70 nm.

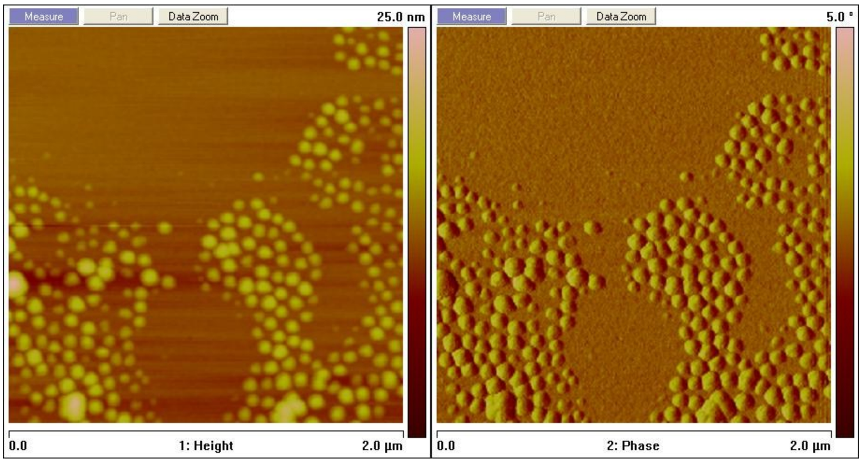


Figure S3. AFM image of SP-WPU emulsion (height and phase image)

3. GPC of SP-WPU

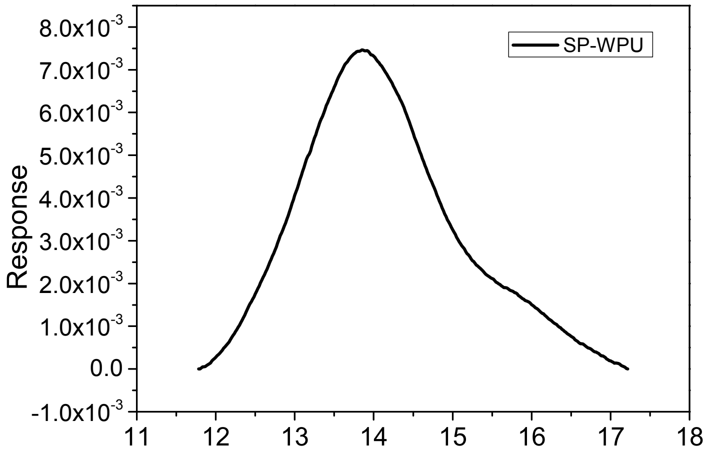


Figure S4. GPC curve of SP-WPU (THF, M_w = 122346, M_n= 33315)

4. The ultra-sonication responsive properties of the SP-PU mixed dispersion

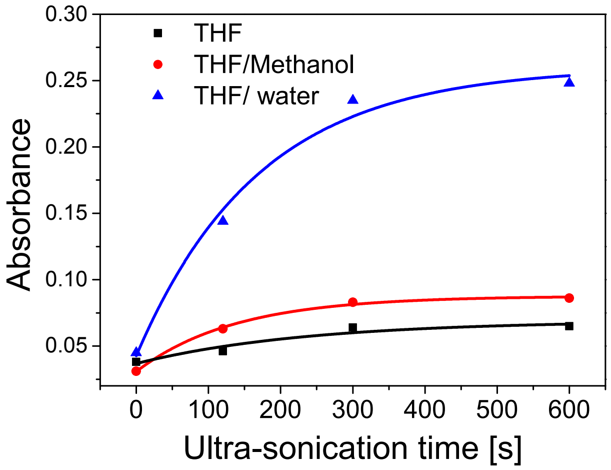


Figure S5. Ultra-sonication responsive properties of the SP-PU mixed dispersion in different mixed solvent. (Black: THF, Red: THF/Methanol, Blue: THF/Water. Water and methanol were controlled at 10 vol %.)

In order to confirm the effect of solvent, another polar solvent methanol, whose polarity is between THF and water, was added into the solution, and the SP-WPU mixed dispersion was also investigated by ultra-sonication experiment. The absorbance at λ_{max} was plotted versus sonication time. THF/Methanol dispersion showed higher intensity than THF/water solution (Figure S5). The intensity of absorbance at λ_{max} increased as the polarity of the mixed solvent increased.

5. Ultra-sonication responsive properties of SP-WPU with different DMPA content.

5.1 Synthesis of SP-WPU with different DMPA content

Table S1. Compositions of SP-WPU with different DMPA

Sample	SP (g)	MDI (g)	IPDI (g)	PTMG (g)	DMPA (g)
1.0 DMPA	0.020 (0.5 mmol)	0.160 (0.64 mmol)	6.446 (29.0 mmol)	10.000 (10.0mmol)	1.340 (10.0mmol)
1.25DMPA	0.020 (0.5 mmol)	0.160 (0.64 mmol)	6.446 (29.0 mmol)	10.000 (10.0mmol)	1.675 (12.5 mmol)
1.5 DMPA	0.020 (0.5 mmol)	0.160 (0.64 mmol)	6.446 (29.0 mmol)	10.000 (10.0mmol)	2.010 (15.0 mmol)

Synthesis of the SP-WPU with different DMPA content was the same as that described in the main text. Different content of DMPA was added after the prepolymer was synthesized. Details of the composition was listed in Table S1.

5.2 Ultra-sonication responsive of samples

The transition degree from SP to MC decreased as the content of DMPA increased. (**Figure S6**) It was attributed to the different structure of the polymer in the mixed solution. TEM (**Figure S7**) showed that the micelle size decreased as the DMPA content increased. It was reported that the formation and swelling of the micelle could enhance the mechanical activation of the polymer. Therefore, mechanical activation of the SP-WPU decreased as the carboxyl group increased.

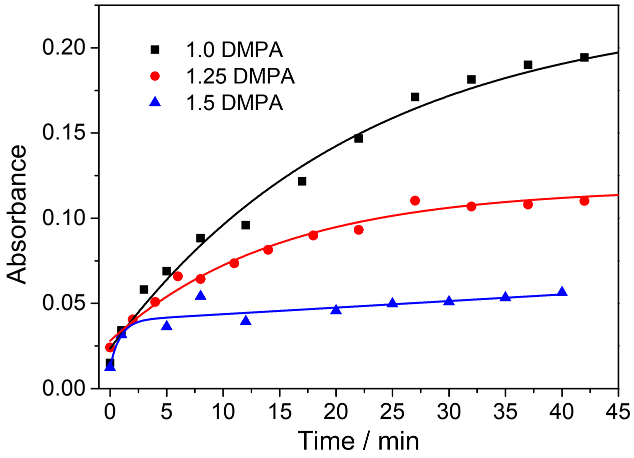
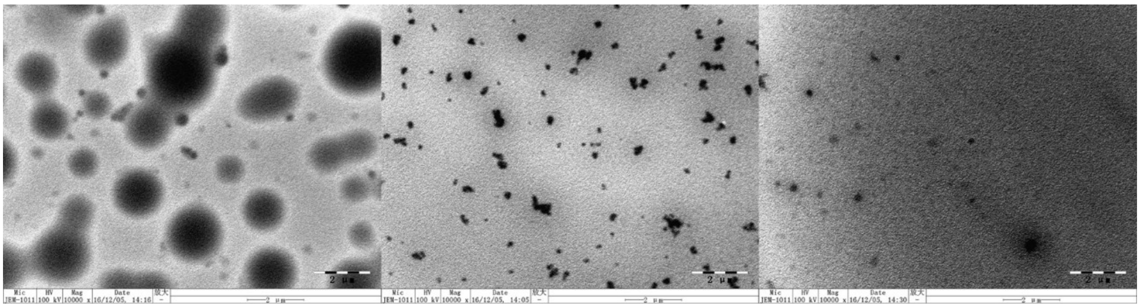


Figure S6. Ultra-sonication activation of SP-WPU with different DMPA content as time evolution.



DMPA 1.0 DMPA 1.25 DMPA 1.5

Figure S7. TEM pictures of SP-WPU with different DMPA content (10 vol% water, scale bar 2 μm)

6. DMA of SP-WPU film

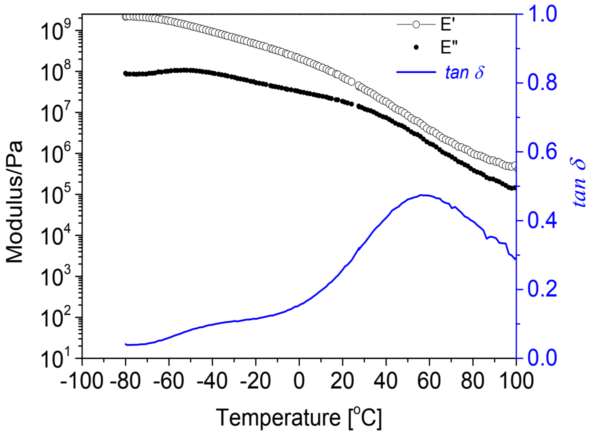


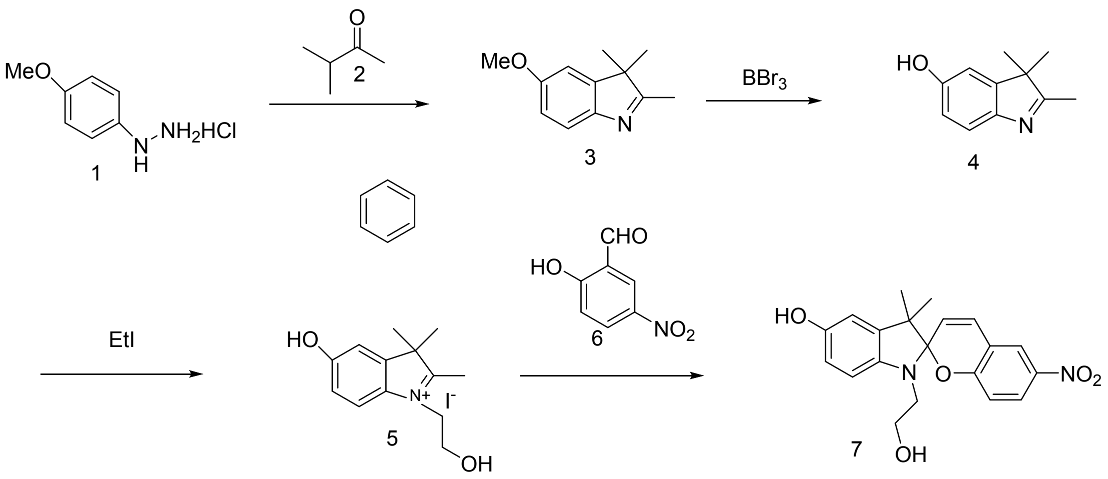
Figure S8. DMA of the SP-WPU film.

The dynamic mechanical tests were carried out on a dynamic mechanical analyzer (DMA) (METRAVIB DMA-450, France). The viscoelastic properties were measured under a nitrogen atmosphere, at a heating rate of 2 K/min from -80 °C to 100 °C and a frequency of 10 Hz. The experiments were carried out until the samples became too soft to be tested. The polyurethane showed microphase separation with soft segment T_g (-45 °C) and hard segment T_g (60 °C) according to the *tan δ* curve. The tensile test was at room temperature, which was below the T_g of the hard segments.

7. Tensile test and UV activation of Control sample

7.1 Synthesis of di-hydroxyl SP in the same side of spiro.

The synthesis of the control sample was followed by the literature[1]. Scheme 2 showed the synthetic procedure of the control spiropyran with two hydroxyl groups on the same side of spiro. Details of the analysis of ^{1}H NMR data was shown in Figure S9. Additionally, control sample of SP-WPU was the same route as that in the main text.



Scheme S2. Synthetic route of a di-hydroxyl spiropyran with functional groups in the same side of spiro ring.

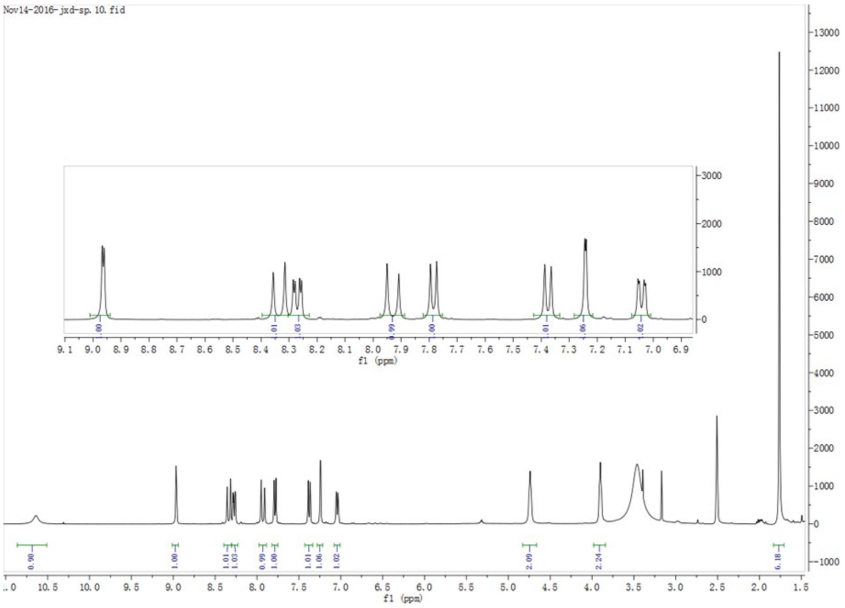


Figure S9. ^{1}H NMR of di-hydroxyl spiropyran with functional groups in the same side of spiro ring.

^{1}H NMR 400 MHz, *d6*-DMSO, HCl): δ 8.96 (d, 1H,Ar-H), 8.32 (d, 1H, Ar-H), 8.26(dd,1H, Ar-H),7.92 (d, 1H, Ar-H), 7.78 (d, 1H, Ar-H), 7.39 (d, 1H, Ar-H),7.25 (d, 1H, Ar-H), 7.04 (dd, 1H, Ar-H), 4.73 (t, 2H, -CH2), 3.89 (, 2H, -CH2), 1.75 (s, 6H,-CH3)

7.2 Stretch and UV activation of the SP-WPU (control sample).

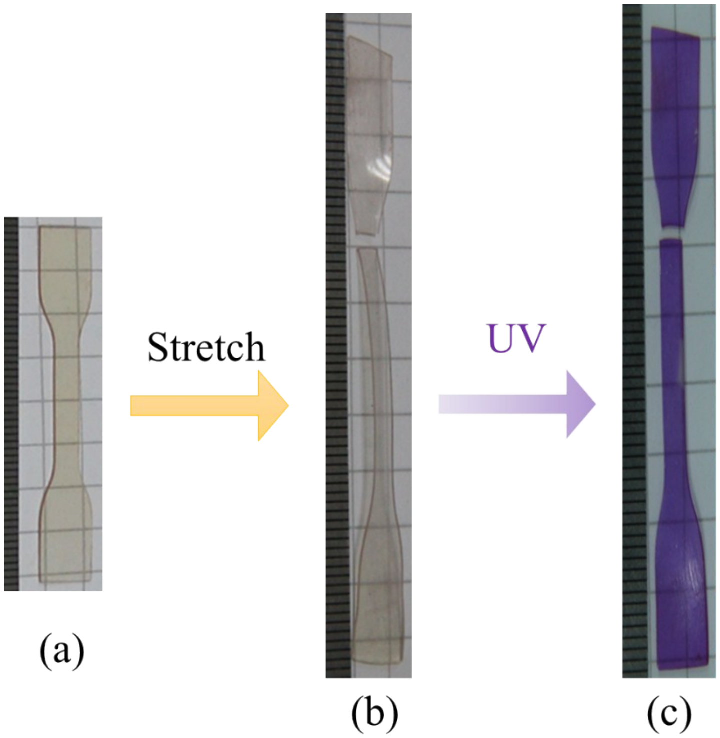


Figure S10. Photos of control sample (a) original shape (b) tensile after break (c) UV lights exposed on the broken sample for 3 min and showed blue color.

1. Lee, C. K.; Davis, D. A.; White, S. R.; Moore, J. S.; Sottos, N. R.; Braun, P. V., Force-Induced Redistribution of a Chemical Equilibrium. *Journal of the American Chemical Society* **2010,** *132* (45), 16107-16111.