Development of Liquid Crystalline Polyurethane Composites with Staging-responsive Shape Memory Effects

Shaojun Chen[a], Jianfeng Ban[*a], Luona Mu[b], Haitao Zhuo[b*],

Supporting Information

1.Experimental section

Text S1: Synthesis of 4,4-Azodibenzoic acid (Azoa):

The experimental details are as follows: 4-Aminobenzoic acid (7.5 g, 0.055 mol), NaOH (25.0 g, 0.625 mol), and H2O (120 mL) were mixed in a 500 mL round-bottomed flask and rigorously stirred at 50 ^{o}C for 25 min to obtain solution A. Glucose (50.0 g, 0.228 mol) was dissolved in 75 mL of H_2O to obtain solution B. Under rigorous stirring at 55 ^{o}C, solution B was slowly added into solution Afor a period of 30 min. The mixture was stirred at 55 ^{o}C for further 8 h. After cooling to room temperature, the pH was adjusted to 6 by adding the dilute acetic acid. The resultant Azoa was precipitated and washed with H_2O. The crude product was purified and at first, dissolved in hot potassium carbonate solution, and then precipitated by adding acetic acid. Finally, the product waswashed with H_2O until the pH reached 7. The target Azoa was obtained as a faint pink solid by filtration and dried at 65°C under vacuum for 24 h to achieve the yield of 80%. The characterization data of the monomer are as follows: Azoa (Figure S1a), 1H NMR (δ,

ppm, DMSO-d6): 12.23 (a, 1H, -COOH), 8.47-7.71 (b, 4H, Ar-H), 6.71 (c, 4H, Ar-H). ppm = 3.33 and 2.67, which belong to the solvent of DMSO-d6.

Text S2: Synthesis of 4-(4-oxyalkyl chain carbonyl) azodibenzoic acid (Azo11) :

The experimental details for the synthesis are as follows: Azoa (5.0 g, 0.018 mol), 1-Bromoundecane (4.35 g, 0.018 mol), K_2CO_3 (7.4 g, 0.054 mol), and KI (0.05 g) were dissolved in 200 mL of absolute ethyl alcohol. Under intense stirring, the solution was heated to 90 ^oC at reflux for 12 h. Subsequently, the solution product was collected by filtration under vacuum, and then the crude solid product was first collected by evaporation under reduced pressure. Thereafter, the obtained product was purified using column chromatography on silica gel with petroleum ether: dichloromethane = 1 : 1 as the eluent. The target Azo11 was obtained as a faint earth yellow solid with the yield of 86%. The characterization data of the monomer are as follows: Azo11 (Figure S1b), 1H NMR (δ, ppm, DMSO-d6): 11.89 (a, 1H, -COOH), 8.07-7.89 (b, 4H, Ar-H), 7.11-6.81 (c, 4H, Ar-H), 4.08 (d, 2H, -OCH_2-), 1.72 (e, 2H, -CH_2-), 1.40-1.04 (f, g, h, i, j, k, l, n, 16H, -CH_2-), 0.83 (m, 3H, -CH_3). ppm = 3.33 and 2.67, which belong to the solvent of DMSO-d6.

2. Supplementary tables and figures

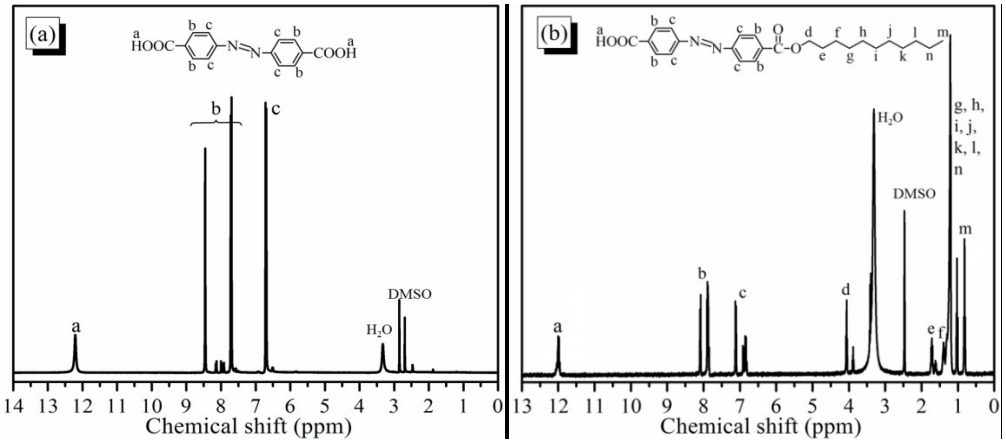

Figure S1 [1]H NMR spectra of (a)Azoa and (b) Azo11 in DMSO-d6.

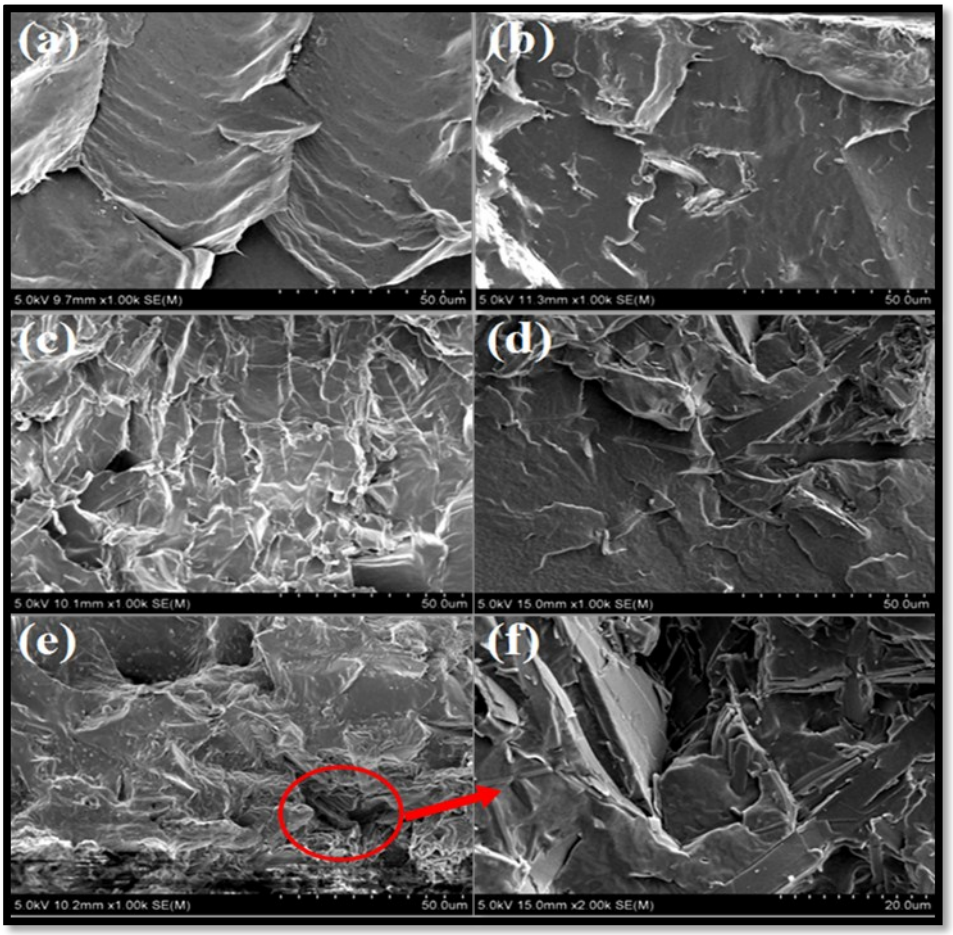

Figure S2 SEM images of (a) PSMPU, (b) P1, (c) P2, (d) P3 (e) P4 and (f) magnified picture of P4, respectively.

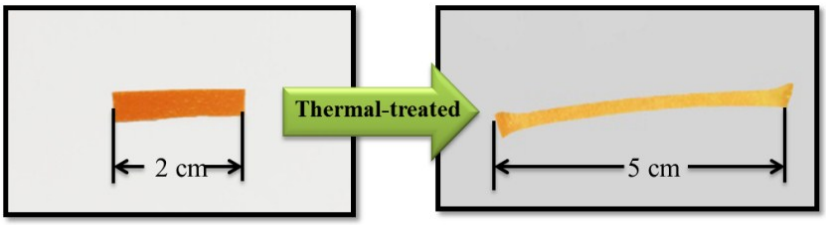

Figure S3 The heating and shape fixed of P3.

Table S1 The shape recovery and shape fixity of PSMPU-Azom composites

Sample	Firstshape recovery ratio (%)	Second shape recovery ratio (%)	First step strain recovery (%)	Second step strain recovery(%)	Total strain recovery (%)
PSMPU	97.05	98.34	61.20	44.45	83.83
P1	100.00	98.89	51.67	45.41	83.11
P2	100.00	98.67	51.23	45.42	83.20
P3	100.00	98.99	52.34	45.19	81.39
P4	100.00	99.81	60.54	47.55	83.77