Electronic Supplementary Material (ESI) for Polymer Chemistry.

Well-Controlled Polymerization of Tri-vinyl Dynamic Covalent Boroxine Monomer: One Dynamic Covalent Boroxine Moiety towards Tunable Penta-Responsive Polymer

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Experimental Procedures

1. Materials and Experimental Section

Materials

THF was distilled from Na/benzophenone prior to use. The azobisisobutyronitrile (AIBN) initiator was recrystallized in methanol. All other solvents and chemicals were used without further purification.

Experimental Section

Synthesis of tri-vinyl dynamic covalent boroxine (DCB) monomer, i.e., 4-vinylphenylboronic acid (VPBA)/tri-vinylphenylboroxine dynamic complex. The tri-vinyl DCB monomer was synthesized as follows: 2.026 g of freshly peeled magnesium scraps (83.3 mmol) were put into a 3-neck round bottom flask. After flame-dried, 10.0 mL (11.6 g, 83.3 mmol) 4-chlorostyrene in 40 mL dry THF was added dropwise. After the reaction was carried out over 3 h, trimethyl borate (16.1 mL, 14.7 g, 142 mmol) in 120 mL dry THF was added to this flask at 0 ℃ through a syringe. When the addition was complete, the reaction was warmed up to room temperature. The solution reacted continually for 4 h under magnetic stirring, and then followed by quenching and hydrolysis with 320 mL of 3.0 N HCl. The mixture was extracted with 200 mL diethyl ether and collected. The organic solution was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The resulting solid was heated in 100 mL water. The mixture was filtered and the supernatants were combined, then stored at 4 ℃ for 10 h. The precipitate was filtered and washed with water, then dried under vacuum overnight at room temperature to afford tri-vinyl DCB monomer as white powder with a yield of 37%. ^{1}H NMR (400 MHz, 5% D_2O/d6-DMSO (v/v), δ): 7.75(d, -C6H4-, 2H), 7.44 (d, -C6H4-, 2H), 6.73 (dd, -CHCH2, 1H), 5.87 (d, -CHCH2, 1H), 5.28 ppm (d,-CHCH2, 1H). Due to the dynamic characteristics of DCB, the molar ratio of VPBA/tri-vinylphenylboroxine changes all the time, depending on the dynamic equilibrium. The molar weight of tri-vinyl DCB monomer is therefore determined to be 834 Da, based on the 1H NMR results in d6-DMSO at 298K, where the molar ratio of VPBA/tri-vinylphenylboroxine is 3: 1.

Dynamic self-assembly of PDCB solution. 20 mg PVPBA was dissolved into 1 mL dry THF, then added 0.9 % of H_2O make up a homogeneous solution , when heated to 50 ^{o}C, the solution exhibits

solution-colloid transition. One drop of colloid deposited on a silica wafer for SEM observation immediately.

2. Characterization Section.

Nuclear Magnetic Resonance (NMR) Spectra.

The ^{1}H NMR spectra were acquired at 298 K using Bruker AscendTM 400 spectrometer operating at 400MHz in CD_3OD or DMSO-d6. The chemical shifts were given in ppm and TMS was used as an internal standard.

Gel permeation chromatography (GPC).

A Viscotek TDA 302 triple detectors (with one TSK-Gel GMHHR-N column), equipped with UV detector, was used for measuring the molecular weight and molecular weight distribution. Purified THF was used as the eluent at a nominal flow rate of 1.0 mL/min and the temperature of measurement was 35 ℃. A GPC calibration curve based on mono-dispersed polystyrene standards was used to calibrate the molecular weight and molecular weight distribution. Polymers were dissolved in THF/H_2O (5 %, v/v) and then reacted with excessive pinacol, prior for GPC characterization.

Dynamic light scattering (DLS).

Malvern Zetasizer Nano ZS-90, equipped with a 633 nm laser source, was used to measure the hydrodynamic size of the nanoparticles in tetrahydrofuran or methanol at a fixed detection angle of 90°.

Transmittance tests of polymer solution in tetrahydrofuran or methanol were acquired at 500 nm wavelength on a Shimadzu UV-2450 spectrometer at 298 K.

Rheological tests.

Thermo Haake MARS rheometer with cone-plate geometry (35 mm) at a fixed gap size of 0.105 mm. In general, the temperature dependence of the storage modulus (G') and lose modulus (G") was tested at fixed frequency of 1.00 rad/s and amplitude of 1 %. For tests at 20 ℃ and 70 ℃, the samples

were heated to the set temperature and then kept at the temperature for 200 seconds. For tests from 70 ℃ to 20 ℃, the samples were cooled at a rate of 3 ℃ /min.

3. Results and Discussion.

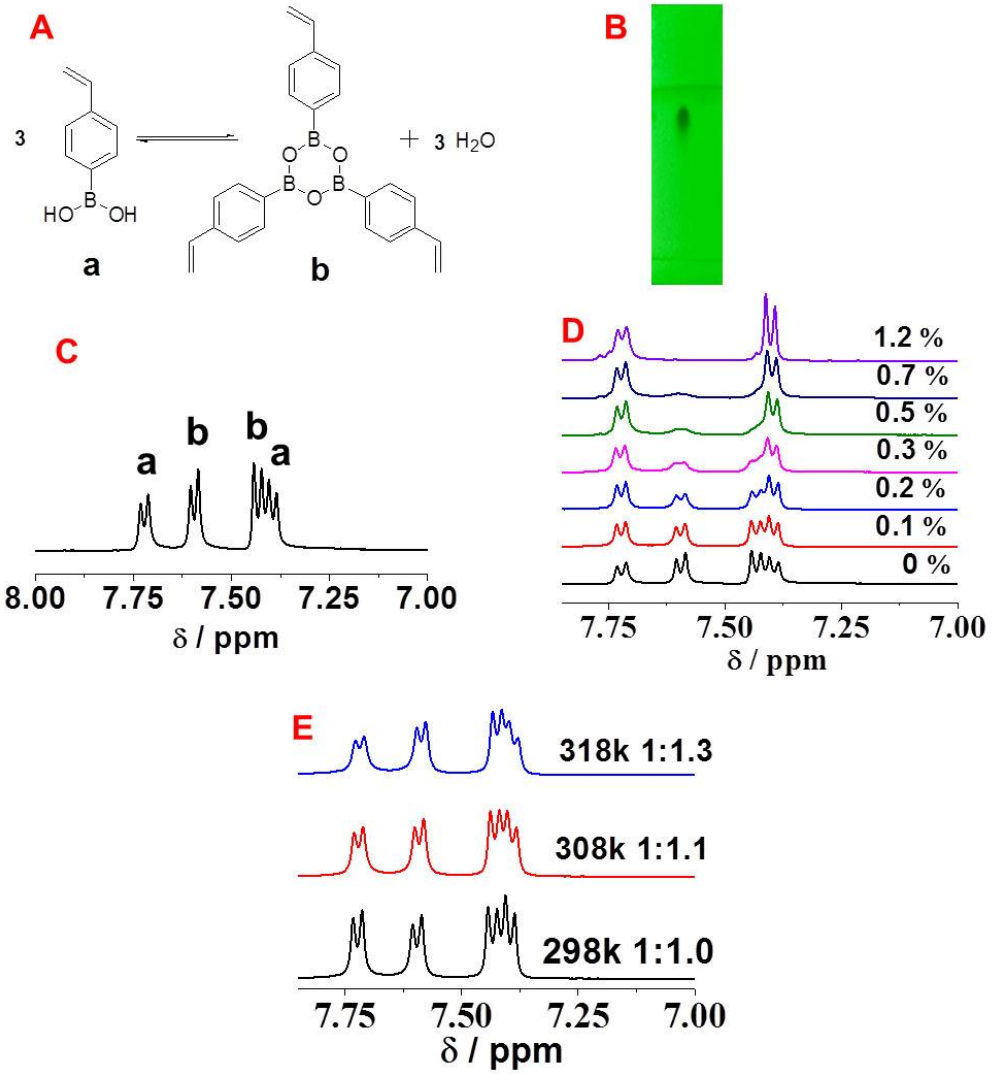

Fig. S1. The illustration of the dynamic characteristics of DCB. (A) illustration of the dynamic chemistry of DCB; (B) digital photo of TLC plate of DCB; (C) ^{1}H NMR spectrum (aromatic region) of DCB in CD_3OD at 298K; (D) ^{1}H NMR spectra (aromatic region) of DCB in CD_3OD with addition of different amounts of D_2O (v/v) at 298K; (E) temperature dependence of ^{1}H NMR spectra (aromatic region, integration ratio of phenyl protons of a/b indicated) of DCB in d6-DMSO.

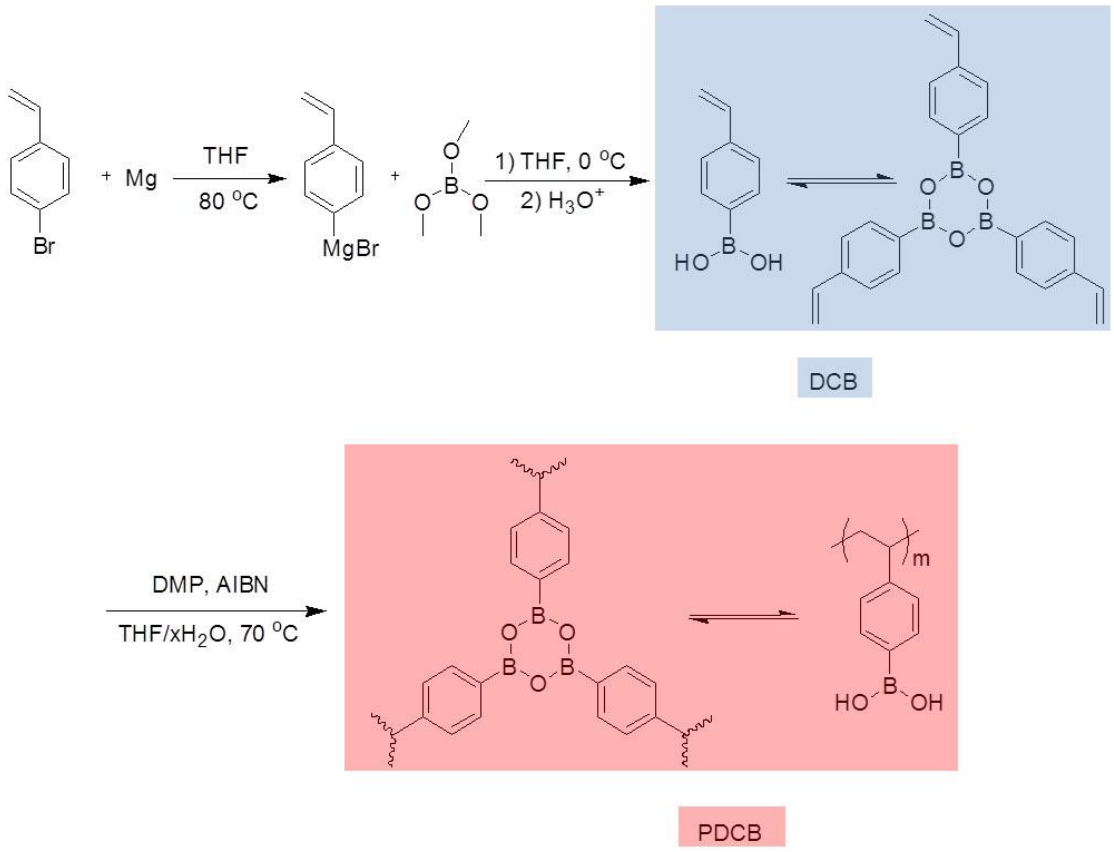

Fig. S2. Illustration of the synthetic route of DCB monomer and corresponding polymer.

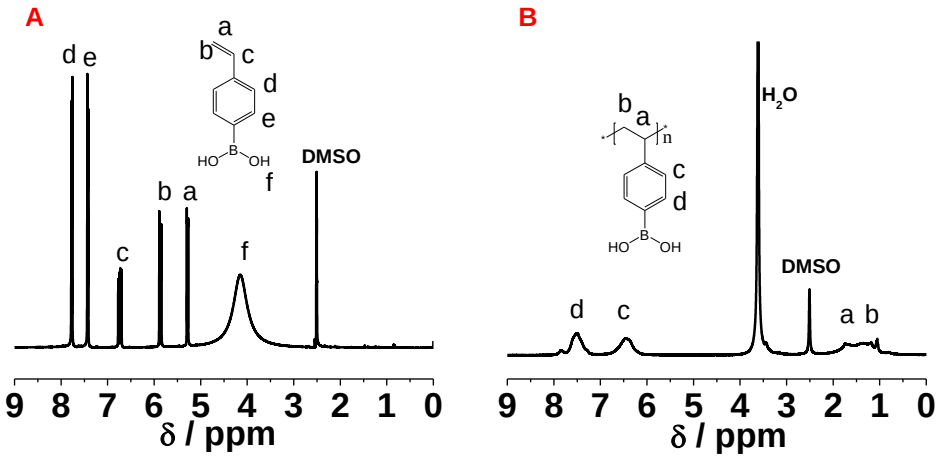

Fig. S3. ^{1}H NMR spectra of hydrolyzed DCB (A) and PDCB (B).

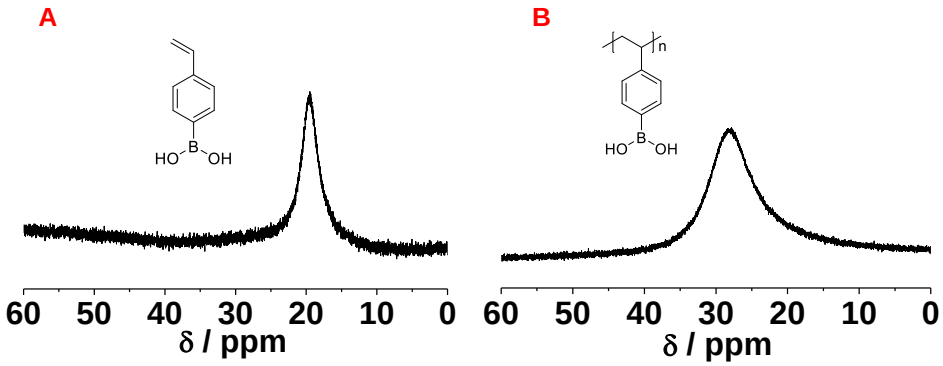

Fig. S4. ^{11}B NMR spectra of hydrolyzed DCB (A) and PDCB (B).

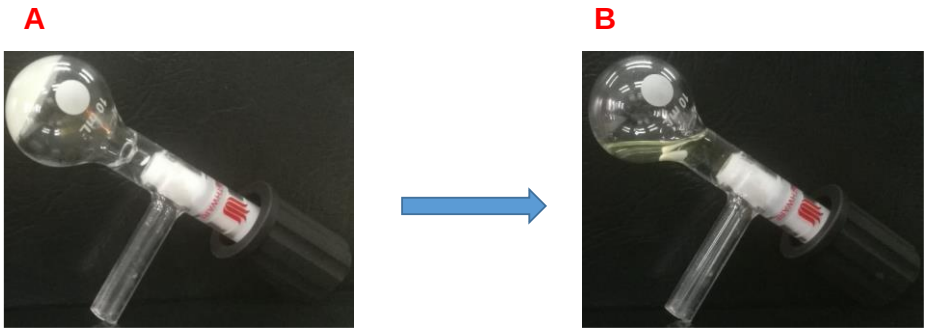

Fig. S5. Digital photos of PDCB polymerization media obtained from polymerization of tri-vinyl DCB in THF containing 2% water. (A) After polymerization at 70 ℃; (B) after cooling to room temperature.

Thermo-responsive polymerization media.MP4

Video 1. Video of the cooling procedure of PDCB polymerization media obtained from polymerization of tri-vinyl DCB in THF containing 2% water.

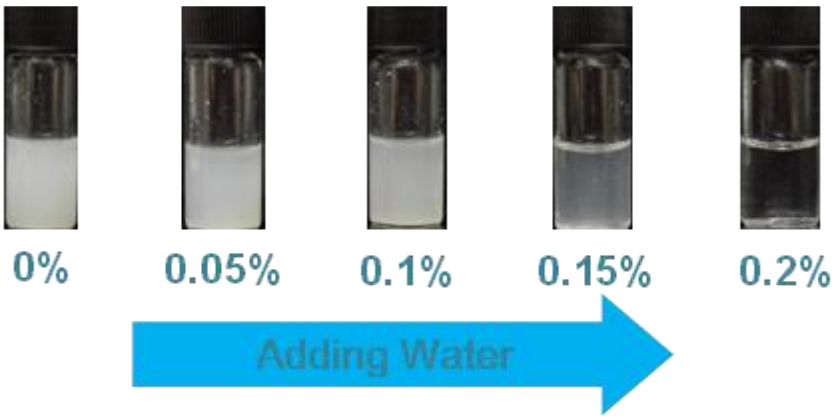

Fig. S6. Digital photos of PDCB solution in methanol ([PDCB]= 20 mg/mL) upon addition of different amounts of water.

Water sensory.mp4

Video 2. Video of the water sensory property of PDCB solution in methanol ([PDCB]= 20 mg/mL) upon addition of 0.2% water (v/v).

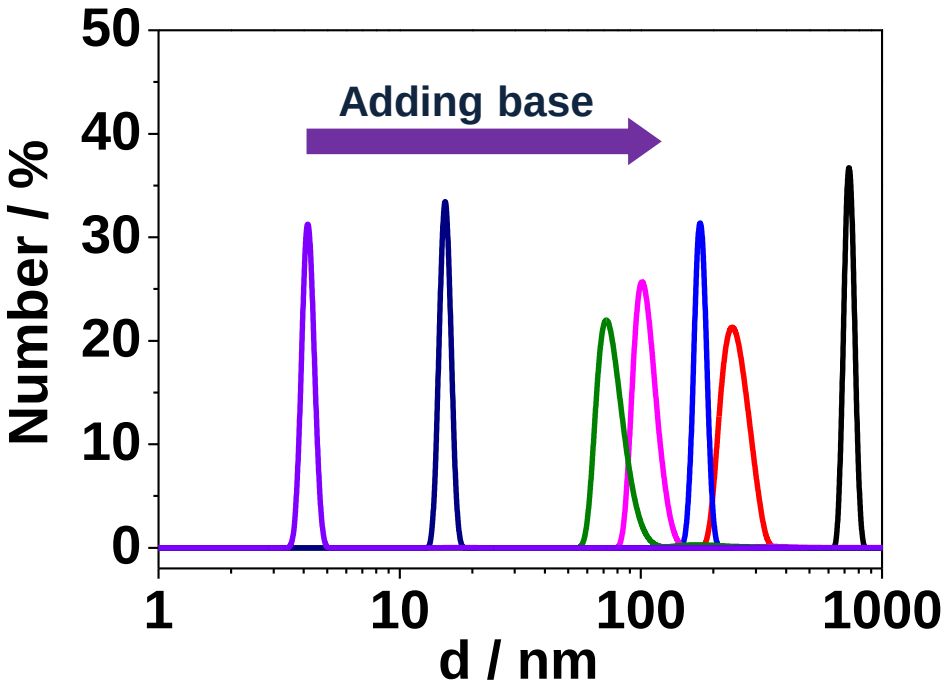

Fig. S7. DLS size distributions of PDCB solution ([PDCB]= 20 mg/mL) in THF with 5% water upon addition of NaOH solution (pH= 14.0).

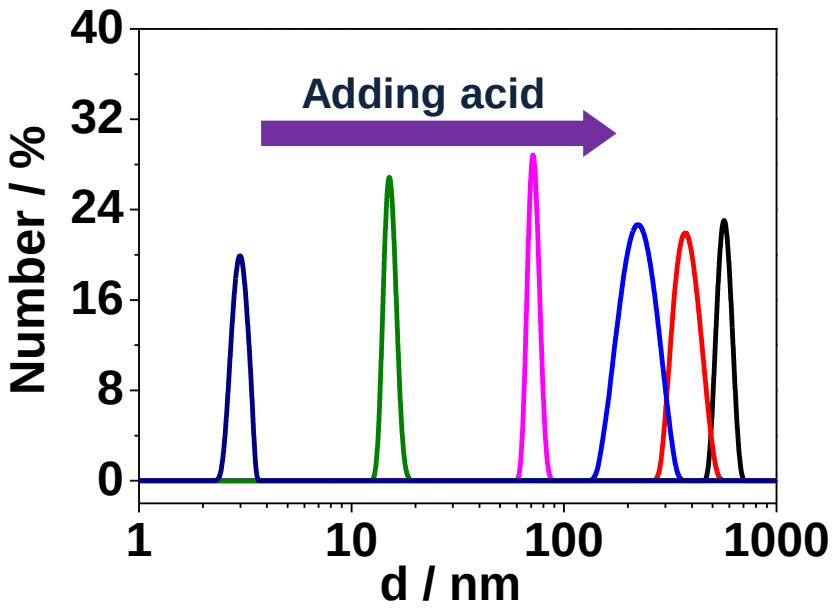

Fig. S8. DLS size distributions of PDCB solution ([PDCB]= 20 mg/mL) in THF with 80% water upon addition of H_2SO_4 solution (pH= 0.0).

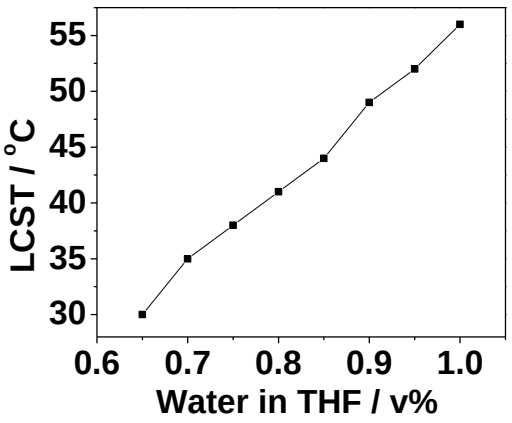

Fig. S9. Plots illustration of the tunable thermo-responsive solution-colloid transition property of PDCB solution ([PDCB]= 20 mg/mL) in THF containing different amounts of water.

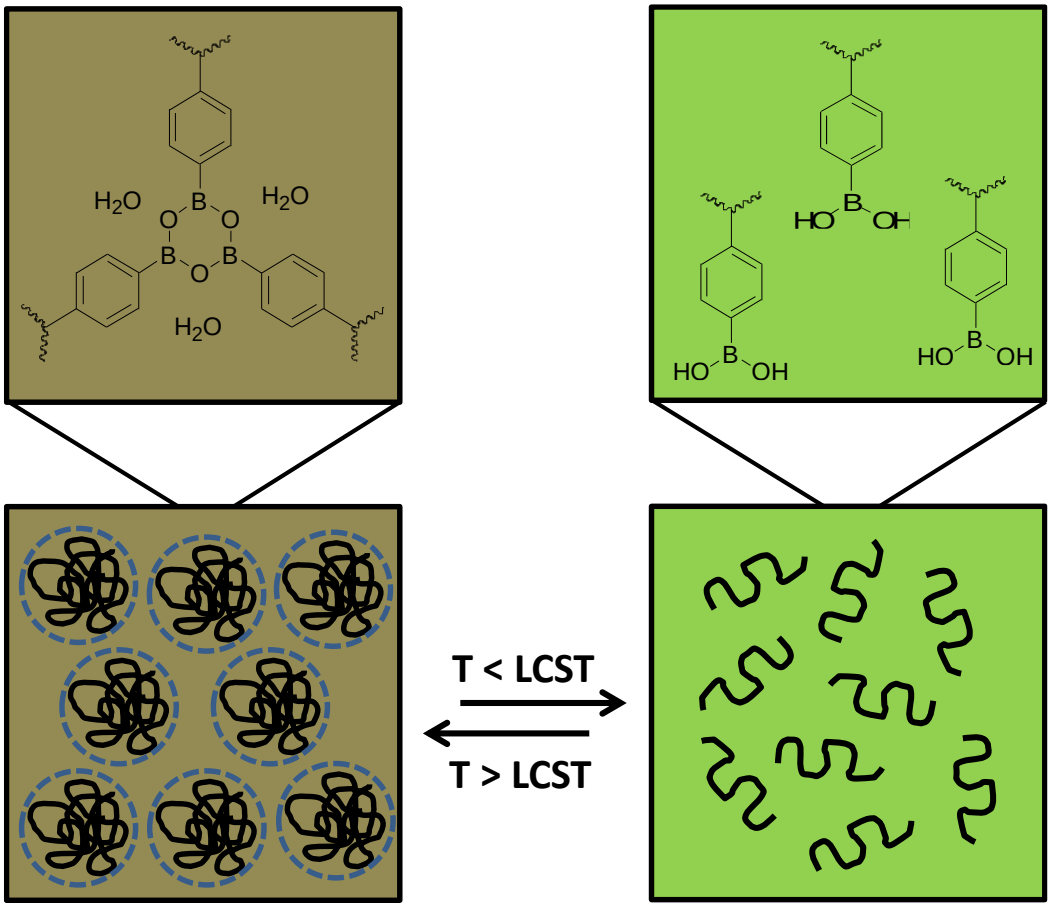

Fig. S10. Illustration of the proposed mechanism of the thermo-responsive solution-colloid transition behavior of PDCB.

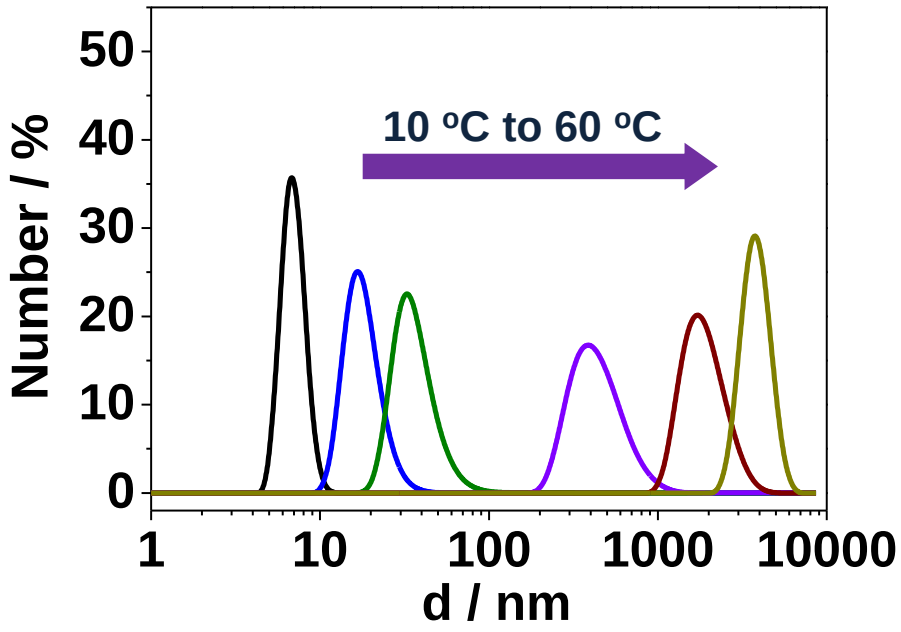

Fig. S11. DLS size distributions of PDCB solution ([PDCB]= 300 mg/mL) in THF containing 1.15% water at different temperatures.

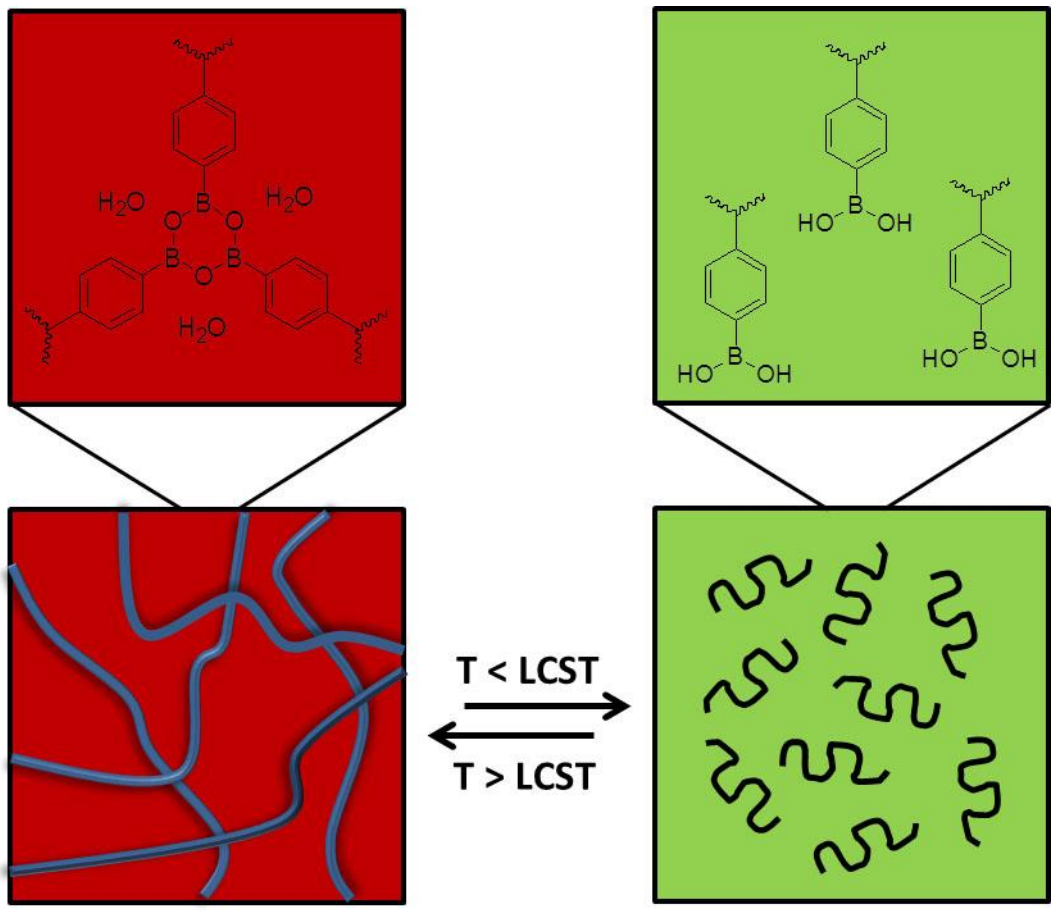

Fig. S12. Illustration of the proposed mechanism of the thermo-responsive sol-gel transition behavior of PDCB.