Supporting Information

for

Structure, Humidity Adaptivity, and Elasticity of Hydrogen-bonding Complexations Formed by Self-assembly of Triblock Copolymer and Homopolymer

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Synthesis of SES triblock copolymers.
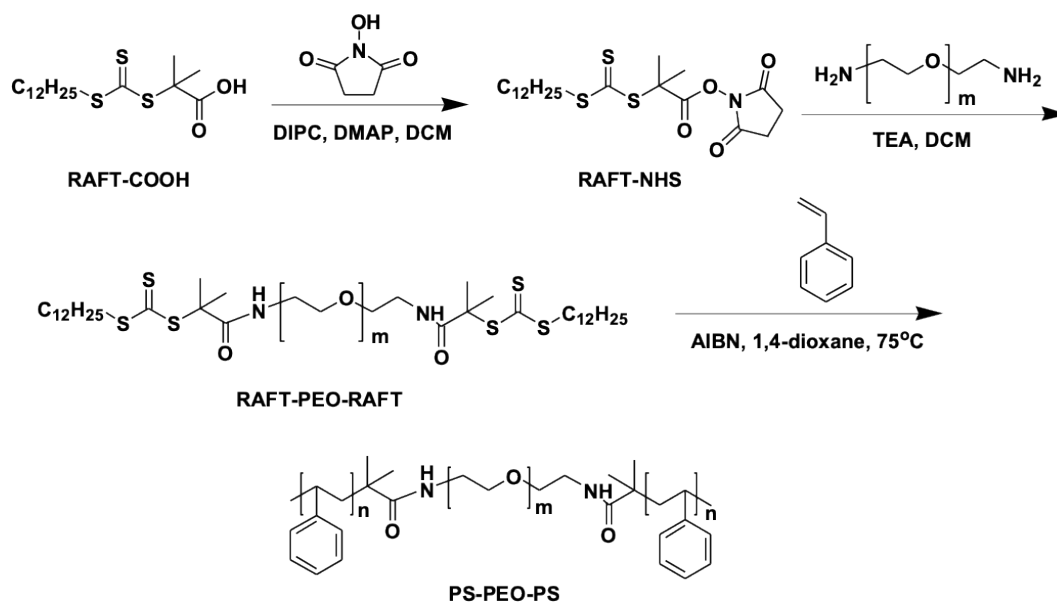
Scheme S1 Synthesis route for SES triblock copolymer.

Materials. Poly(ethylene oxide) (NH$_2$-PEO$_{40k}$-NH$_2$) (M_n = 40 kg mol^{-1}, PDI = 1.01) was purchased from Sinopeg Chemical Reagent Co. N-hydroxysuccinimide (NHS, 98%, aladdin), 4-dimethylaminopyridine (DMAP, 98%, Adamas), N,N′-diisopropylcarbodiimide (DIPC, 98%, Adamas), diethyl ether (99%, Greagent), triethylamine (TEA, 99.5%, Greagent), 1,4-dioxane (99.5%, Greagent), petroleum ether (PE, 95%, b. p. 60-90 °C, Greagent), and ethyl acetate (EA, 99.6%, Greagent) were used as received. 2, 2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Macklin) was recrystallized three times with ethanol before using. Dichloromethane (DCM, 99%, Greagent) was dried over CaH$_2$ and then distilled into the solvent storage bottle for later use. Styrene (99%, Macklin) was passed a basic alumina column to remove the polymerization inhibitor. S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (RAFT-COOH) was synthesized according to the reported reference.[1]

Characterization. ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) spectra were acquired

using CDCl$_3$ as solvent (99% D, J&K Chemicals) with a Bruker 600 MHz NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton impurities in CDCl$_3$ at δ 7.27 ppm. Gel Permeation Chromatography (GPC) was performed using Waters Instrument (515/2410/2487) with THF as the eluent at a flow rate of 1.0 mL min^{-1} at 40 °C and using polystyrenes as standards.

Synthesis of RAFT-NHS. RAFT-COOH (10 g, 27.43 mmol), NHS (3.80 g, 33.00 mmol) and DMAP (0.34 g, 2.75 mmol) were dissolved in 30 mL anhydrous DCM, and cooled to 0 °C in an ice-bath. DIPC (4.16 g, 33.00 mmol) was slowly added with a syringe. The mixture was stirred at room temperature for 12 h. When the reaction was finished, the crude product was purified by column chromatography on a silica gel column using a mixture of solvent PE and EA (5 : 1, v/v). After removal of the solvent by a rotary evaporator, the product of yellow powder RAFT-NHS was collected with a yield of 80%. ^{1}H NMR (600 MHz, CDCl$_3$, ppm, δ): 3.30-3.32 (t, 2H), 2.82 (s, 4H), 1.88 (s, 6H), 1.66-1.72 (m, 2H), 1.26-1.40 (m, 18H), 0.88-0.90 (t, 3H).

Synthesis of PEO-based macromolecular chain transfer reagent (RAFT-PEO$_{40k}$-RAFT). NH$_2$-PEO$_{40k}$-NH$_2$ (4 g, 0.1 mmol) and RAFT-NHS (3.70 g, 8 mmol) were dissolved in 30 mL anhydrous DCM. Then 0.5 mL of TEA was added to the solution. The mixture was stirred at room temperature for over 48 h. The reaction was detected by ^{1}H NMR. When the reaction was reached, the solvent was concentrated with a rotary evaporator, and precipitated it three times in 500 mL cooled ether to remove the unreacted RAFT-NHS. The precipitation was collected as slight yellow powder with the yield of 85%. ^{1}H NMR (600 MHz, CDCl$_3$, ppm, δ): 3.64 (s), 1.69 (s), 1.26-1.40 (m), 0.88-0.90 (t).

Synthesis of PS$_n$-PEO$_{40k}$-PS$_n$ triblock copolymers. RAFT-PEO$_{40k}$-RAFT (1 g, 0.025 mmol), initiator AIBN (0.016 g, 0.01 mmol), monomer styrene (5 mL, 43.6 mmol) and 5 mL 1,4-dioxane as the solvent were introduced into a 25 mL Schlenk bottle. The flask was degassed with freeze-pump-thaw three times to remove the oxygen, and then placed it in a 75 °C oil bath for polymerization. When the polymerization was completed, the flask was quenched with liquid nitrogen. The crude product was precipitated into cooled ether three times to thoroughly remove the unreacted styrene monomer. And the white powder was obtained after filtration. By controlling the reaction time and monomer concentration, triblock copolymers with different molecular weights were obtained. The detail information of triblock copolymer was listed in **Table S1**.

Table S1 Molecular weight, polydispersity index, PS contents, PEO and PS glass transition temperatures of SES triblock copolymers.

sample	PS $M_{n,NMR}{}^{a}$ (g mol^{-1})	PS-PEO-PS $M_{n,NMR}{}^{a}$ (g mol^{-1})	PDI^{b}	PS%^{a} (wt%)	PEO^{c} Tg (°C)	PS^{c} Tg (°C)
PS$_{4k}$-PEO$_{40k}$-PS$_{4k}$	8 k	48 k	1.23	16.67	- 44	-
PS$_{7k}$-PEO$_{40k}$-PS$_{7k}$	14 k	54 k	1.29	25.93	- 44	97
PS$_{10k}$-PEO$_{40k}$-PS$_{10k}$	20 k	60 k	1.32	33.33	- 44	101
PS$_{18k}$-PEO$_{40k}$-PS$_{18k}$	36 k	76 k	1.52	47.37	- 44	104

^{a} Molecular weight calculated based on ^{1}H NMR. ^{b} Molecular polydispersity index measured by GPC. ^{c} Molecular thermal behaviors measured by DSC.

Discussions on SES synthesis. The detail synthesis procedure of PS$_n$-*b*-PEO$_{40k}$-*b*-PS$_n$ triblock copolymer is shown in **Scheme S1**. First, RAFT-NHS was used to react with NH$_2$-PEO$_{40k}$-NH$_2$ to prepare the RAFT-PEO$_{40k}$-RAFT macromolecular RAFT reagent. Then, the

target tri-block copolymer of PS_n-PEO_{40k}-PS_n with various PS content were polymerized by controlling the reaction time and the monomer concentration. ^1H NMR spectra (**Figure S1**) and GPC evolution curves (**Figure S2**) can well prove the correctness of the chemical structure of each molecule. From the ^1H NMR spectra we can see, for the small molecule RAFT-NHS intermediates, the chemical shift of -CH_2-CH_2- in NHS group is appeared at 2.82 ppm (**Figure S1 a**). The single peak at 3.64 ppm is the chemical shift of proton -O-CH_2-CH_2- in PEO chain (**Figure S1 b**). Compared with **Figure S1 a**, the characteristic chemical shift of proton -S-C$(CH_3)_2$- in the RAFT-NHS is shifted from 1.88 ppm to 1.69 ppm, which can confirm that the RAFT-PEO_{40k}-RAFT macromolecular RAFT reagent is correctly obtained. In **Figure S1 c**, the broader peaks from 6.44 to 7.10 ppm and 1.27 to 1.84 ppm are the signals of proton of benzene ring and -CH_2-CH- in polystyrene blocks. On the GPC evolution curves (**Figure S2**), the evolution curves of four samples are unimodal, indicating these molecules are monodisperse, which further proving the accuracy of the target molecular structure. The detail of molecular information of PS-PEO-PS triblock copolymer is summarized in **Table S1**.

Supporting figure
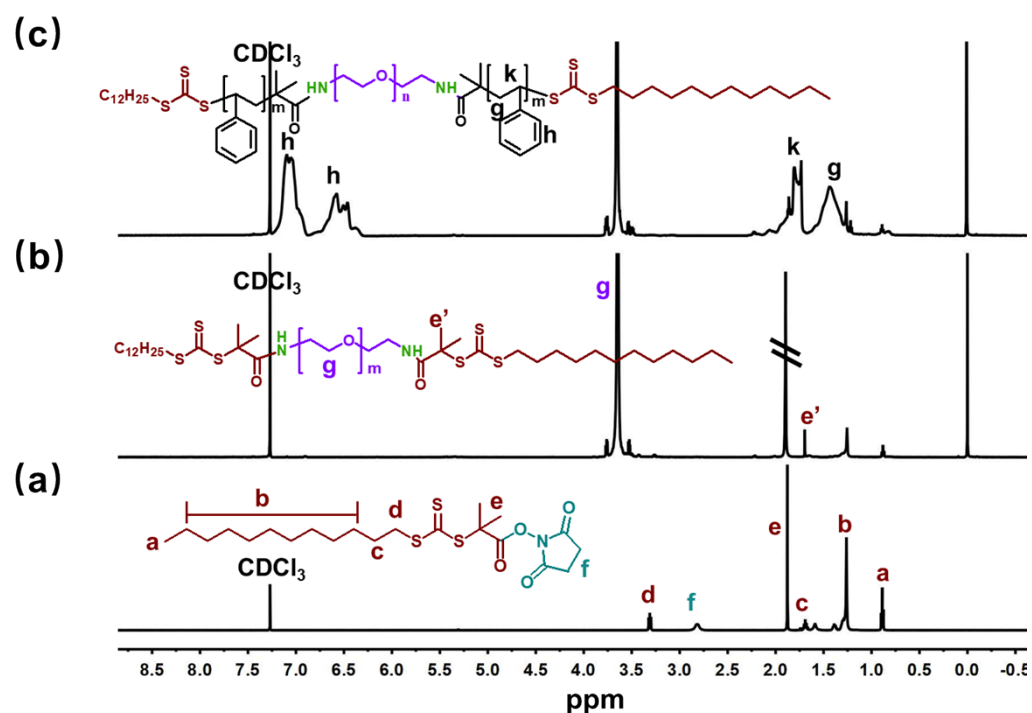
Figure S1 ^{1}H NMR spectra of **a)** RAFT-NHS, **b)** RAFT-PEO-RAFT, **c)** PS-PEO-PS and their corresponding assignments.
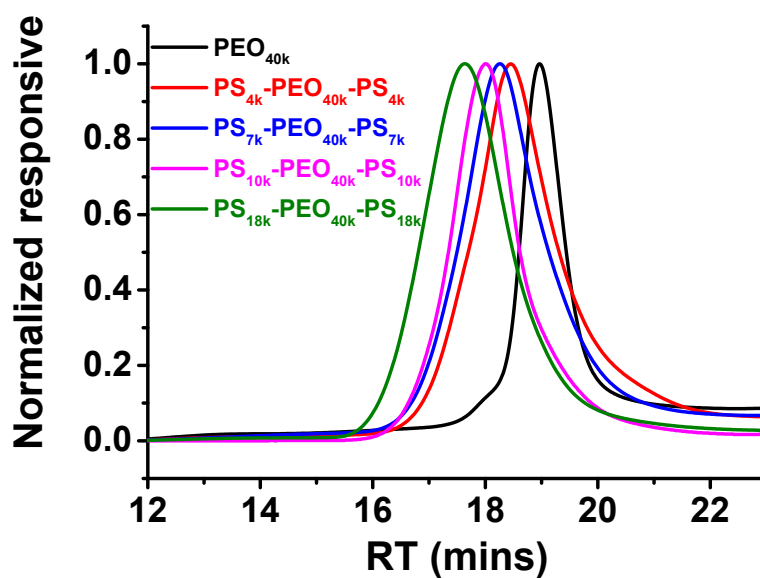

Figure S2 GPC curves of triblock copolymers with different molecular weight.
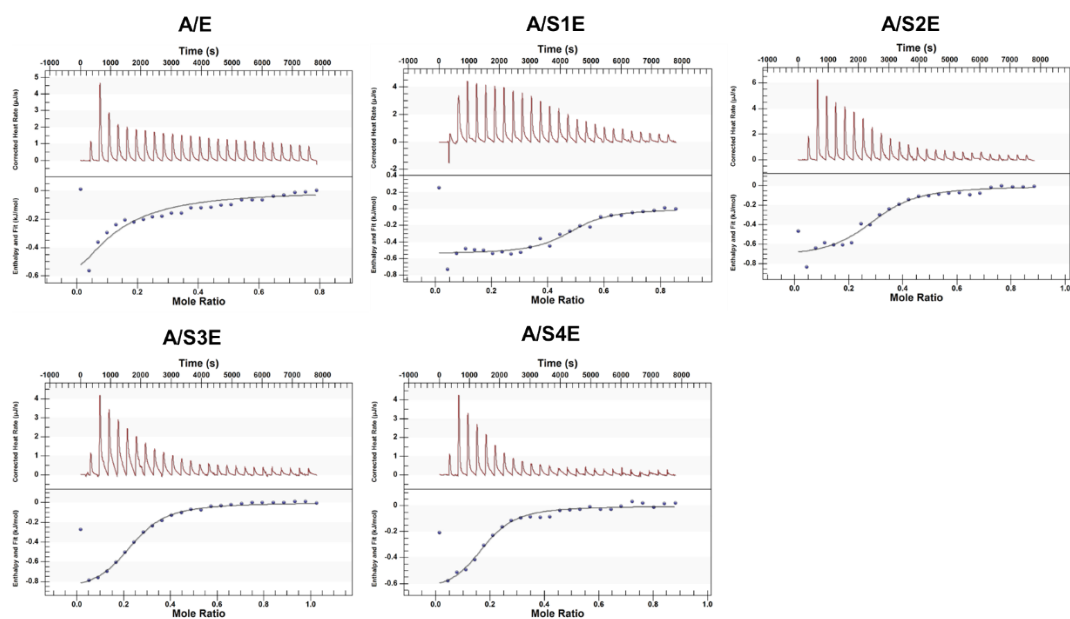
Figure S3 ITC results illustrate the formation of hydrogen-bonds between PAA and SES in DMF solvent. When the hydrogen-bond is formed, an exothermic peak is shown. The results indicate all samples can form hydrogen-bonds in DMF solvent.
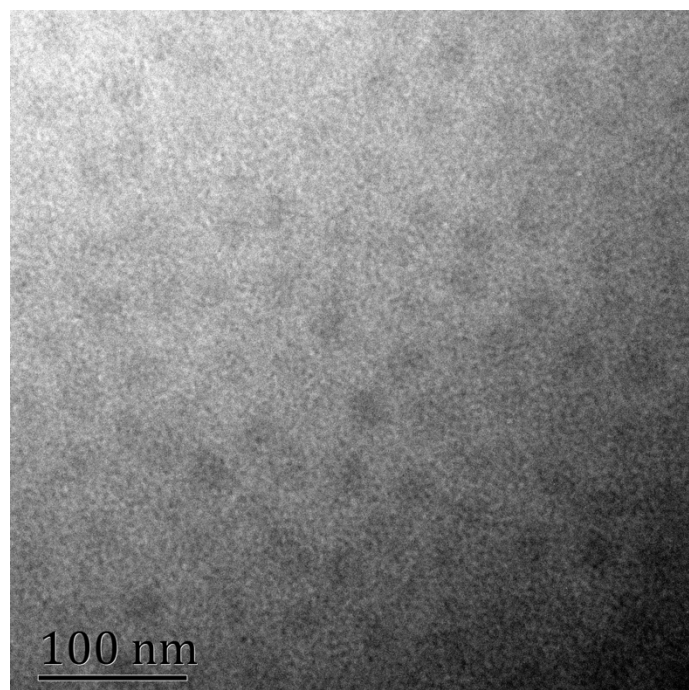

Figure S4 Transmission Electron Microscopy (TEM) photograph of A/S4E.
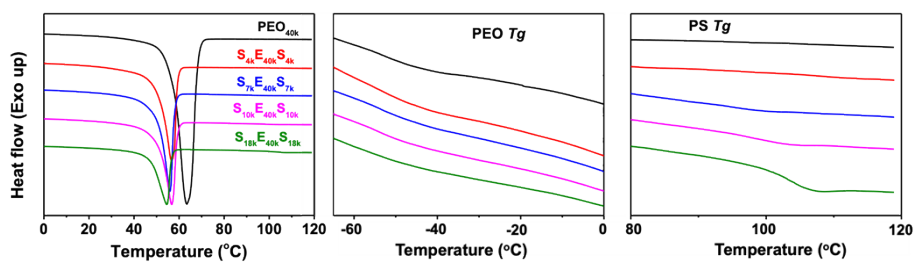
Figure S5 DSC curves of PEO and SES triblock copolymers.
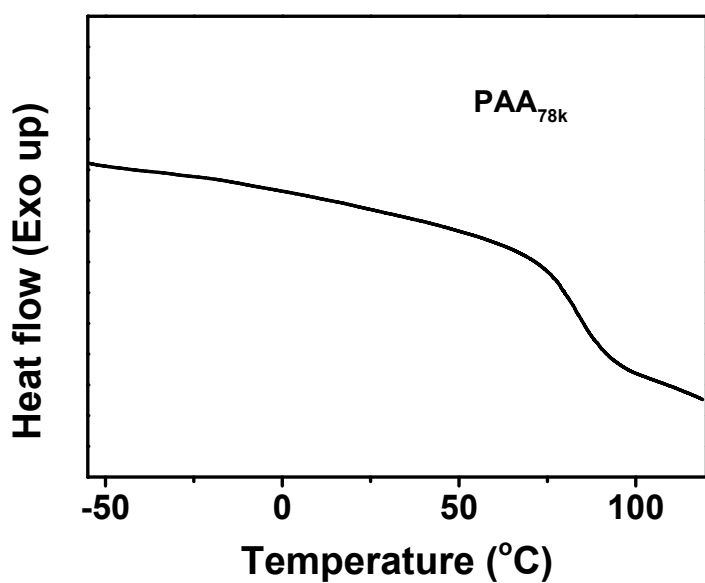
Figure S6 DSC curve of PAA_{78k}.
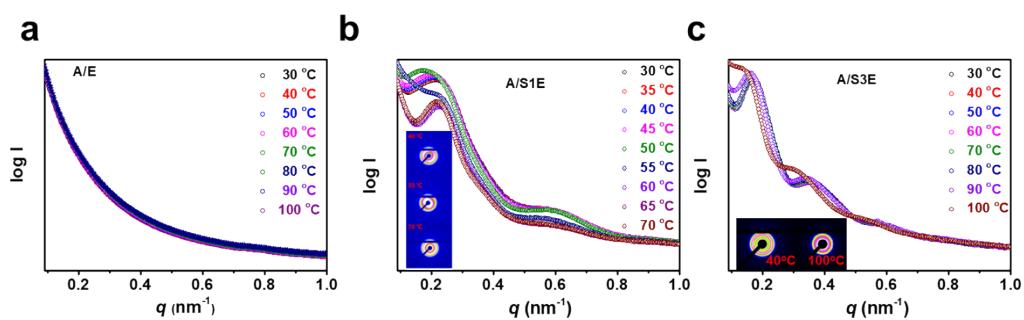
Figure S7 Temperature dependent SAXS curves of **a)** A/E, **b)** A/S1E, and **c)** A/S3E.
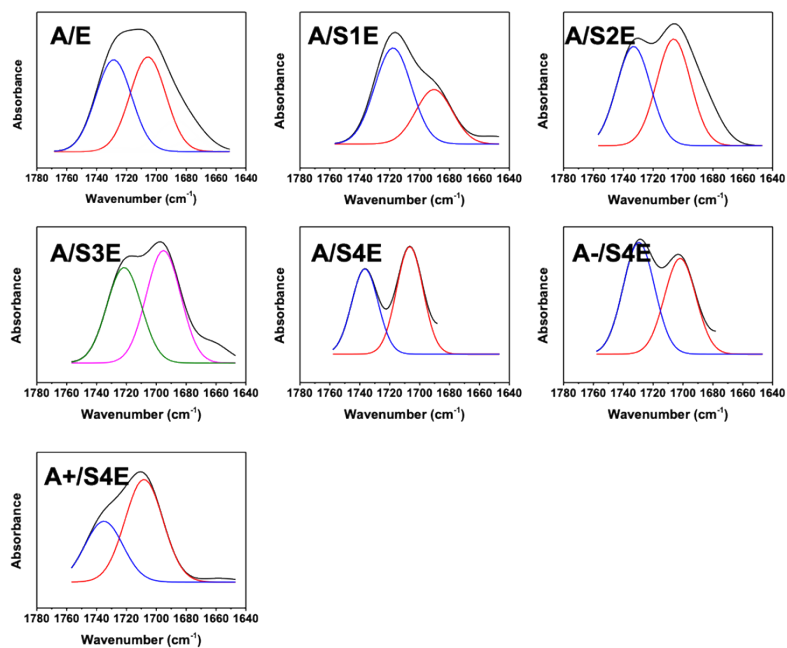
Figure S8 The peak shift of C=O FT-IR absorbance using Gaussian fit.
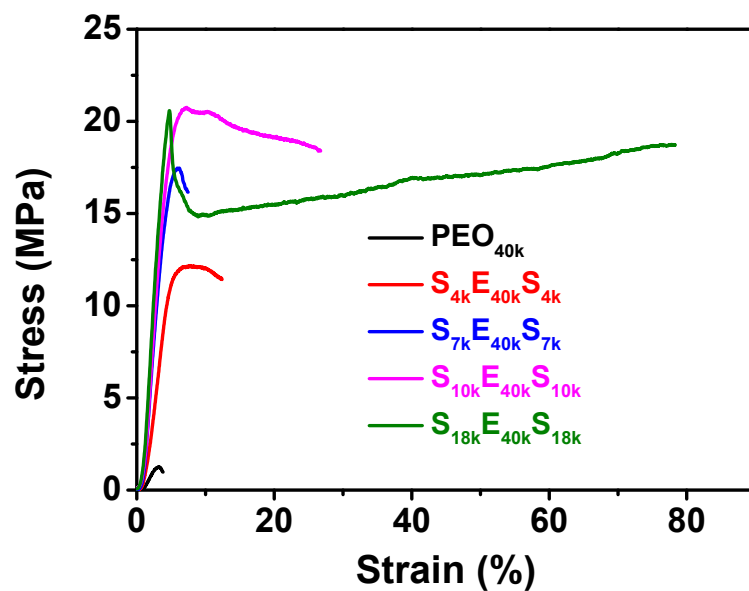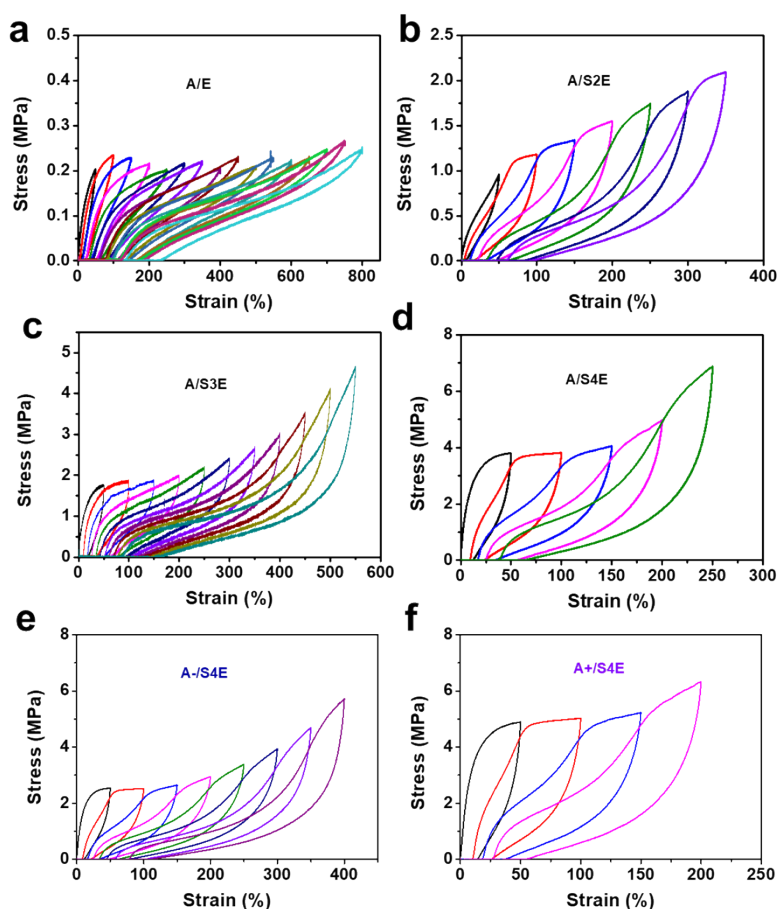

Figure S9 Stress-strain curves of SES triblock copolymers.

Figure S10 Step cyclic loading-unloading curves of complexations tested at 25 °C and 40%

RH condition. Each cycle strain increases by 50% and until the sample break. **a)** A/E, **b)**

A/S2E, **c)** A/S3E, **d)** A/S4E, **e)** A-/S4E, and **f)** A+/S4E. The cross-linked A/E presents lower

strength but longer breaking elongation. The complexations crosslinked by the PS hard

sphere show increased breaking strength and good elasticity. However, the chain length of

PAA would affect the mechanical and elastic properties of complexations. A-/SE with lower

PAA chain length exhibits flexibility and increased elastic properties, while A+/SE with longer PAA chain shows plastic mechanical properties.
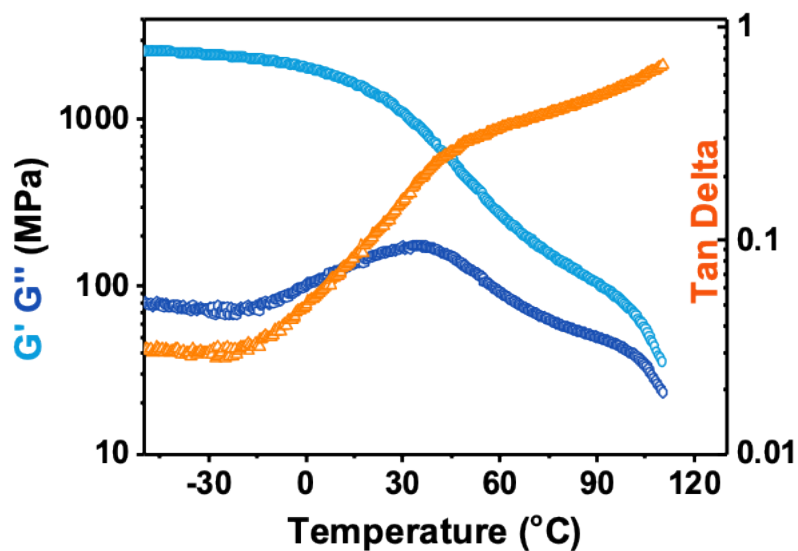

Figure S11 Temperature dependent DMA test of A/S3E. The sample was dried before testing. The heating rate was 10 °C/min.
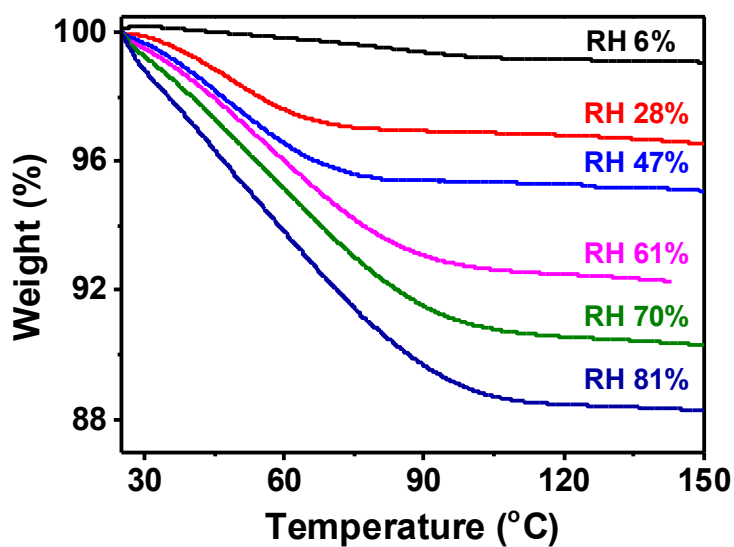

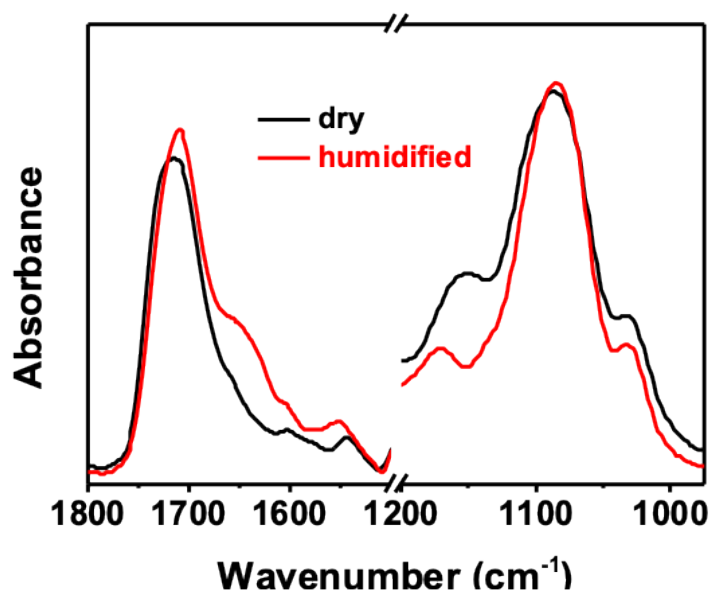**Figure S12** TGA curves of A/S3E incubated with different humidity at 25 °C.

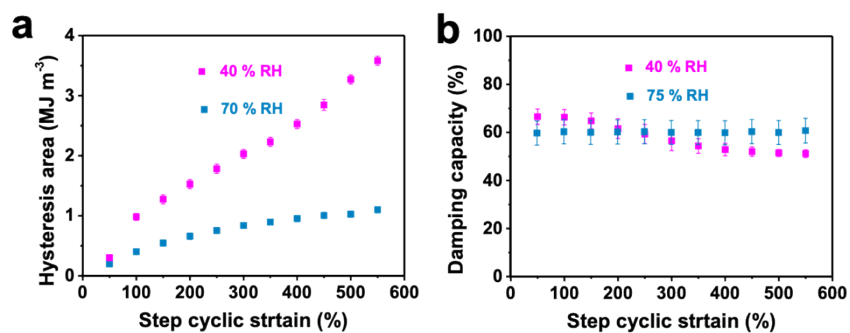**Figure S13** FT-IR spectra of A/S3E at dry and humidify treatment state.

Figure S14 The **a)** hysteresis area and **b)** damping capacity of A/S3E at different RH conditions which were calculated from Figure 5a and 5b.

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Referrence:

1. Lai, J. T.; Filla, D.; Shea, R., Functional polymers from novel carboxyl-terminated trithiocarbonates as highly efficient RAFT agents. *Macromolecules* **2002,** *35*, 6754.