Supporting Information for:

Modulating Mechanical Properties of Self-assembled Polymer Networks by Multi-functional Complementary Hydrogen Bonding

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General. All reagents were purchased either from Acros Organics, Aldrich or Strem Chemicals and used without further purification unless otherwise noted. Grubbs first generation catalyst was purified by filtration using purified benzene under an atmosphere of argon. Spacer monomer (**1**), thymine monomer (**2**), cyanuric acid monomer (**3**), diaminotriazine crosslinking agent (**4**), ditopic Hamilton wedge crosslinking agent (**5**), monotopic 2,4-diaminotriazine (**6**), monotopic Hamilton wedge (**7**) and **Poly-13** were synthesized according to published procedures.[1] ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were taken using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Gel-permeation chromatography (GPC) analyses were carried out using a Shimadzu pump, a Shimadzu UV detector with tetrahydrofuran (THF) as the eluant and a set of American Polymer Standards columns (100, 1,000, 100,000 Å linear mixed bed). The flow rate used for all the measurements was 1 mL/min. All GPC measurements were calibrated using poly(styrene) standards and were carried out at room temperature. M_w, M_n and PDI represent the weight-average molecular weight, number-average molecular weight and the polydispersity index respectively. Rheological measurements were carried out on an MCR300 rheometer (Anton Paar), equipped with Peltier elements and evaporation blocker that enable measurements at elevated temperature in a cone-plate geometry (diameter 50mm, angle 1°). All measurements reported here were carried out in oscillatory mode in order to probe the equilibrium structures of the polymer solutions without applying shear flow.

Polymerizations

Poly-12: Monomers **1** (1.890 g, 7.56 mmol) and **2** (349.86 mg, 0.84 mmol) were dissolved in 30 mL of $CHCl_3$. A stock solution of Grubbs' first generation initiator was prepared in $CHCl_3$ and an amount of the stock solution equaling 6.91 mg ([M]/[I] = 1000:1) of the initiator was added to the monomer solution. The solution was stirred at room temperature and the reaction was monitored by observing the olefinic signals of the monomer by ^{1}H NMR spectroscopy. Upon complete conversion after 6 hours, a drop of ethyl vinyl ether was added to terminate the polymerization, followed by prolonged drying at room temperature under high vacuum for 24 hours to remove all the solvent.

GPC data of Poly-12

Entry	mol % of 2	[M]/[I]	M_n (10^{-3})	M_w (10^{-3})	PDI
Poly-12	10	125	46	71	1.56
Poly-12	10	1000	240	320	1.32

Table S-1. GPC data of the unfunctionalized **Poly-12** in THF at room temperature.

Poly-123: Monomers **1** (1.80 g, 7.2 mmol), **2** (562 mg, 1.34 mmol) and **3** (188 mg, 0.44 mmol) were dissolved in 30 mL of $CHCl_3$. A stock solution of Grubbs' first generation initiator was prepared in $CHCl_3$ and an amount of the stock solution equaling 7.40 mg ([M]/[I] = 1000:1) of the initiator was added to the monomer solution. The solution was stirred at 40 °C and the reaction was monitored by observing the olefinic signals of the monomer by ^{1}H NMR spectroscopy. Upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization, followed by prolonged drying at 60 °C to remove all the solvent.

GPC data of Poly-123

Entry	mol % of 2	mol % of 3	[M]/[I]	M_n (10^{-3})	M_w (10^{-3})	PDI
Poly-123	10	10	125	94	65	1.4

Table S-2. GPC data of unfunctionalized **Poly-123** using THF as the eluent.

Self-assembly experiments of the thymine system

We studied the hydrogen bonding self-assembly between model compounds which consisted of the monomer **2** and the monotopic compounds **6** and **7**, using ^{1}H NMR spectroscopy. We probed the self-assembly by monitoring the shifting of the amine proton signal of **6,** amide proton signals of **7** and the imide proton signal of monomer **2** before and after self-assembly. The self-assembly was performed using a 0.2 M solution of the compounds in deuterated chloroform. The imide signal of **2** shifted downfield from 9.47 ppm to 12.98 ppm upon the addition of one equivalent of monotopic **6**, while the amine proton signals of **6** shifted downfield from 5.83 ppm to 7.44 ppm. Further addition of another three equivalents of **6** resulted in the downfield shift of the imide proton to 13.60 ppm, whereas the amine proton signal of **6** was shifted to 5.97 ppm. The imide signal of monomer **2** shifted downfield from 9.47 ppm to 11.81 ppm upon the addition of half equivalent of monotopic wedge **7,** while the amide proton signals of **7** shifted downfield from 8.76 ppm and 8.53 ppm to 9.93 ppm and 9.57 ppm respectively. Further addition of another half equivalent of **7** resulted in the downfield shift of the imide proton of **2** to 12.23 ppm, whereas the amide proton signal of **7** was shifted to 9.56 ppm and 8.89 ppm. These results demonstrate the strong hydrogen bonding interactions between monomer **2** with **6** and **7**.

Self-assembly experiments of competitive hydrogen bonding interactions

Before conducting crosslinking studies, the competitive hydrogen bonding between monomer **3** and the monotopic compounds **6** and **7** was investigated. Using ^{1}H NMR spectroscopy, the chemical shifts of the amine proton signal of **6**, the amide proton signals of **7** and the imide proton signals of **3** before and after self-assembly were monitored. These self-assembly experiments were performed using a 0.2 M solution of the compounds in deuterated chloroform and corrected for solvent dilution effects. First we studied the self-assembly of **3** with **6**. Upon the addition of two equivalents of **6**, the imide signal of **3** shifted downfield from 9.78 ppm to 13.81 ppm, while the amine proton signals of **6** shifted downfield from 5.33 ppm to 5.74 ppm. Addition of one equivalent of **5** resulted in the downfield shifts of the imide protons of **3** to 13.40 ppm and the amine protons of **6** to 5.80 ppm, whereas the amide protons of **7** shifted from 8.64 and 8.14 ppm to 9.07 and 8.61 ppm respectively. Addition of another equivalent of **7** resulted in the imide proton of **3** to shift to 13.27 ppm, whereas the amide proton signals of **7** were shifted to 8.97 and 8.56 ppm. Control complexation experiments for **7** with **6** and **3** with **7** were also carried out. It can be concluded from the chemical shifts listed in Table 3 that the addition of **7** to the complex formed between **3** and **6** results in decomplexation of cyanuric acid-2,4-diaminotriazine multi-point hydrogen bonded complex, as was hypothesized.

Compound	shifts in (ppm)	Compound	shifts in (ppm)
3	9.78^c	**5** + 2 Eq. **6**	8.74^w & 8.26^w, 5.66^d
6	5.33^d	**3** + 2 Eq. **6**	13.81^c, 5.74^d
7	8.64^w & 8.14^w	(**3** + 2 Eq. **6**) + **7**	13.40^c, 5.80^d, 9.07^w & 8.61^w
3 + **7**	13.24^c, 9.46^w & 9.03^w	(**3** + 2 Eq. **6**) + 2 Eq. **7**	13.27^c, 5.74^d, 8.97^w & 8.56^w

Table S-3. ^{1}H NMR spectroscopy shifts of small molecule compounds upon hydrogen bonded

self-assembly. Symbols: *c* represents the imide protons of **3**, *d* represents amine protons of **6** and

w represents the amide protons of **7**.

Rheological analyses

For all crosslinking experiments, the polymers were dissolved in a calculated amount of 1-chloronaphthalene and the mixture was stirred overnight at room temperature to ensure a homogenous solution. Then, a calculated amount of the crosslinking agent was added and the mixture was stirred briefly at elevated temperature until a homogenous solution was obtained. The sample was then allowed to rest at room temperature for twelve hours before the rheological experiments were carried out. The preparation of **Poly-123-4** is described as a representative example: **Poly-123** (170 mg, 0.12 mmol based on the hydrogen bonding functional groups along the polymer backbone) was dissolved in 1.53 g of 1-chloronaphthalene (10 weight %). Then 36 mg (0.12 mmol based on the hydrogen bonding sites allowing for quantitative crosslinking) of **4** was added to the sample and the suspension was heated until a clear homogenous solution was obtained. The polymer solution was then allowed to rest at room temperature for least twelve hours before rheological measurements were carried out.

The rheological testing protocol of all polymer solutions consisted of: 1) strain amplitude sweep at constant frequency (temperature 20°C; strain amplitude $\gamma = 0.001$-10, angular frequency $\omega = 6.28$ rad/s) to confirm linear viscoelastic regime, 2) frequency sweep at constant strain amplitude (20°C; $\gamma = 0.01$; $\omega = 0.1$-100 rad/s) to determine network viscoelasticity, 3) temperature sweep (20 to 80°C; $\gamma = 0.1$; $\omega = 6.28$ rad/s) to characterize thermal stability, 4) frequency sweep (80°C; $\gamma = 0.1$; $\omega = 0.1$-100 rad/s), 5) temperature sweep (80 to 20°C; $\gamma = 0.01$; $\omega = 6.28$ rad/s) to investigate thermal reversibility, 5) frequency sweep at constant strain amplitude (20°C; $\gamma = 0.1$; $\omega = 0.1$-100 rad/s) to determine thermal recovery.

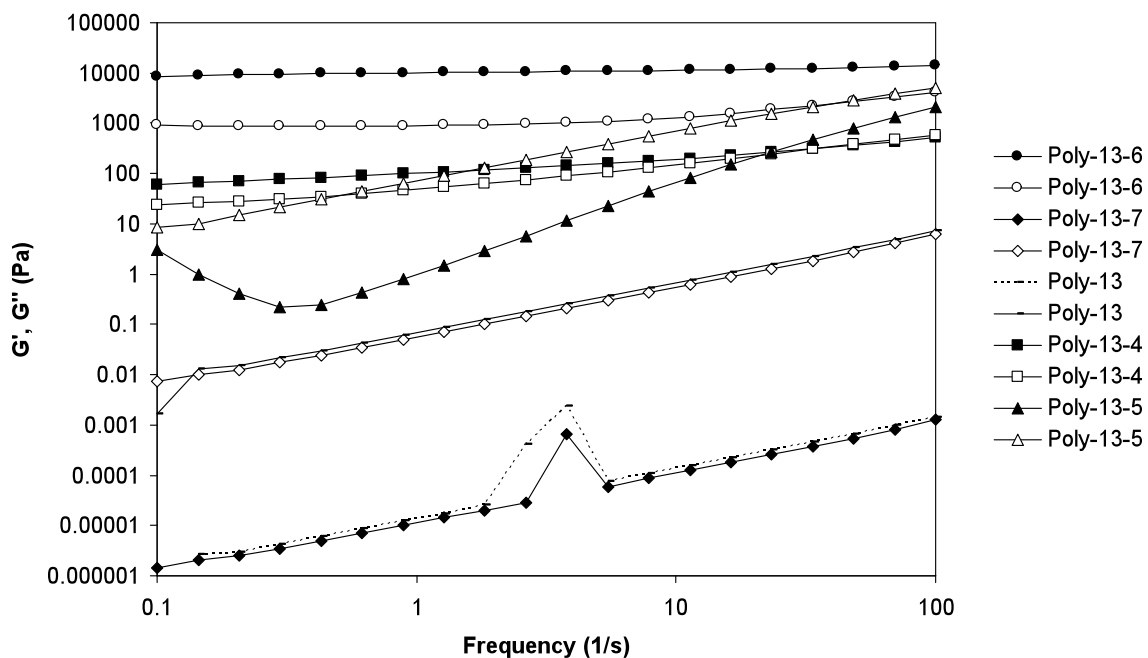**Cyanuric acid system** (1 eq of all crosslinkers)

Figure S-1. Frequency sweep profile of **Poly-13** (dash), **Poly-13-4** (squares), **Poly-13-5** (traingles), **Poly-13-6** (circles) and **Poly-13-7** (diamonds) at strain amplitude of 0.1. Filled symbols represent the elastic modulus, whereas the empty symbols represent the loss modulus.

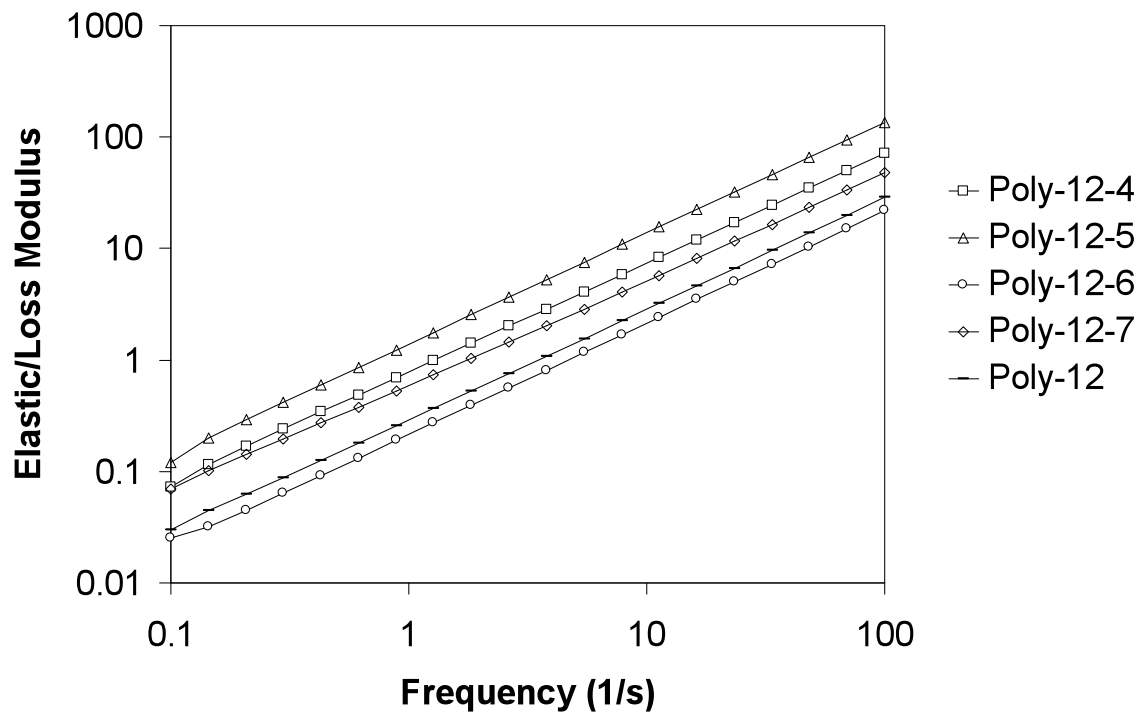**Thymine system** (1 eq of all crosslinking agents)

Figure S-2. Frequency sweep profile of **Poly-12** (dash), **Poly-12-4** (squares), **Poly-12-5** (triangles), **Poly-12-6** (circles) and **Poly-12-7** (diamonds) at strain amplitude of 0.1. The empty symbols represent the loss modulus. Only loss modulus profile is depicted as the **Poly-12** system has very low elastic moduli.

Terpolymer

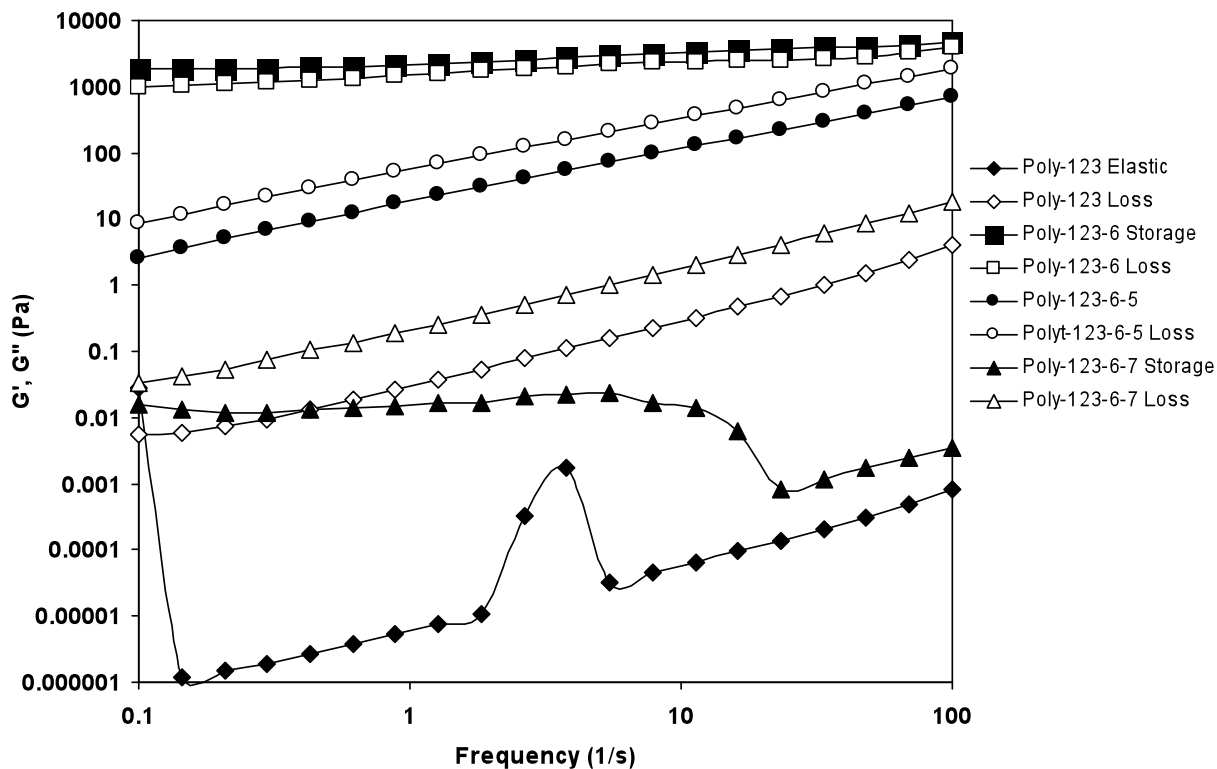Crosslinking-decrosslinking profiles of **Poly-123**

Figure S-3. Frequency sweep profile of **Poly-123** (diamonds), **Poly-123-6** (squares), **Poly-123-6-5** (circles), and **Poly-123-6-7** (triangles). Filled symbols represent the elastic modulus, whereas the empty symbols represent the loss modulus.

References

(1) Nair, K. P. B., Breedveld, V.; Weck, M. *Macromolecules* **2008**, *41*, 3429-3438.