

# Supporting Information:

## Distinguishing Relaxation Dynamics in Transiently Crosslinked Polymeric Networks

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## Materials and Instrumentation

### Materials

Hydroxyethylcellulose (HEC) of different molecular weights were purchased from Aldrich and dried overnight in a vacuum oven at 60 °C. The degree of substitution (DS) and molar substitution (MS) on commercial HEC1300 were 1.5 and 2.5, respectively, however, the exact DS and MS for HEC90 and HEC250 samples were unknown. 2-naphthyl isocyanate, dibutyltin dilaurate, 4-vinylbenzyl chloride, 4,4'-bipyridine, 4,4'-azobis(4-cyanovaleric acid) and vinylben-

zyl(trimethylammonium) chloride were purchased from Aldrich and used as received. Cucurbit[8]uril (CB[8]),<sup>1</sup> MV-NCO,<sup>2</sup> Dbf-NCO and Pyr-NCO<sup>3</sup> were prepared according to literature procedures.

## Instrumentation

<sup>1</sup>H-NMR (500 MHz) spectra was recorded using a Bruker Avance BB 500 and <sup>1</sup>H-NMR (400 MHz) was carried out using an Avance III HD Smart Probe spectrometer. Chemical shifts were recorded in ppm ( $\delta$ ) in D<sub>2</sub>O with the internal reference set to  $\delta = 4.79$  ppm. ATR FT-IR spectroscopy was conducted using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory.

Rheological characterisations were performed using a Discovery Hybrid Rheometer (DHR-2), a controlled stress hybrid rheometer from TA Instruments fitted with a water bath set to various temperatures. All measurements were performed using a 40-mm parallel plate geometry with a gap of 500 nm and the results were analysed using TA Instruments' TRIOS software. Dynamic oscillatory strain amplitude sweep measurements were conducted at a frequency of 10 rad s<sup>-1</sup>. Dynamic oscillatory frequency sweep measurements were conducted at a 1% strain amplitude, between 0.01 to 100 rad s<sup>-1</sup>. Temperature sweeps were carried out on a ramp at a rate of 1°C min<sup>-1</sup> between 10 and 70°C.

Gel permeation chromatography (GPC) was carried out in water (H<sub>2</sub>O) on a Shodex glucose column with a Shimadzu SPD-M20A prominence diode array detector, Optilab refractive index detector and dynamic light scattering detector (both Wyatt). Before injection, the samples were filtered through 0.2  $\mu$ m PVDF filters using a 0.5 mL min<sup>-1</sup> flow rate.

Scanning Electron Microscopy (SEM) images were obtained using a Leo 1530 variable pressure SEM and InLens detector. The SEM samples were prepared by direct freezing of the supramolecular polymer networks in liquid nitrogen followed by lyophilisation. The resulting cryo-dried soft matrixes were imaged after Au sputtering.

## Experimental

### Synthesis of HEC-Np

HEC (1.00 g) was dissolved in N-methylpyrrolidone (NMP, 150 mL) at 110°C overnight. The solution was cooled to room temperature, 2-naphthyl isocyanate (Np-NCO, 29.7 mg, 0.18 mmol) and dibutyltin dilaurate (TDL, 3 drops) were added and the mixture stirred at room temperature overnight. The functional polymer was then purified by precipitation from acetone, filtered, dialysed for three days (MWCO 15 kDa) and obtained by lypholisation (1.01 g, 98%). <sup>1</sup>H-NMR Spectroscopy (D<sub>2</sub>O, 500 MHz):  $\delta$  (ppm) = 8.0 - 7.3 (7H, br, Np), 4.5 - 2.9 (307H, br, cellulose backbone). Elemental analysis: Found C, 46.76; H, 6.95; N, 0.21. C<sub>215</sub>H<sub>367</sub>O<sub>151</sub>N<sub>1</sub> required C, 47.98; H, 6.83; N, 0.26. FT-IR (ATR) = 3410 (br), 2950 (br), 2910 (br), 1395, 1075 (s) cm<sup>-1</sup>. GPC (H<sub>2</sub>O): For HEC1300\*5Np M<sub>n</sub> (PDI) = 1.07 x 10<sup>6</sup> g mol<sup>-1</sup> (1.1); HEC250\*5Np M<sub>n</sub> (PDI) = 3.73 x 10<sup>5</sup> g mol<sup>-1</sup> (1.1); and HEC90\*5Np M<sub>n</sub> (PDI) = 1.45 x 10<sup>5</sup> g mol<sup>-1</sup> (1.2).

### Synthesis of HEC-Dbf

HEC1300 (1.00 g) was dissolved in N-methylpyrrolidone (NMP, 150 mL) at 110°C overnight. The solution was cooled to room temperature, dibenzofuran isocyanate (Dbf-NCO, 49 mg, 0.21 mmol) and dibutyltin dilaurate (TDL, 3 drops) were added and the mixture stirred at room temperature overnight. The functional polymer was then purified by precipitation from acetone, filtered, dialysed for three days (MWCO 15 kDa) and obtained by lypholisation (1.00 g, 97%). <sup>1</sup>H-NMR Spectroscopy (D<sub>2</sub>O, 500 MHz):  $\delta$  (ppm) = 7.9 - 7.3 (9H, br, Dbf), 4.6 - 2.8 (455H, br, cellulose backbone). FT-IR (ATR) = 3395, 2875, 1655, 1353, 1055, 888 cm<sup>-1</sup>. GPC (H<sub>2</sub>O): M<sub>n</sub> (PDI) = 1.07 x 10<sup>6</sup> g mol<sup>-1</sup> (1.1).

## Synthesis of HEC-Pyr

HEC1300 (1.00 g) was dissolved in N-methylpyrrolidone (NMP, 150 mL) at 110°C overnight. The solution was cooled to room temperature, dibenzofuran isocyanate (Dbf-NCO, 52 mg, 0.21 mmol) and dibutyltin dilaurate (TDL, 3 drops) were added and the mixture stirred at room temperature overnight. The functional polymer was then purified by precipitation from acetone, filtered, dialysed for three days (MWCO 15 kDa) and obtained by lyophilisation (0.98 g, 97%). <sup>1</sup>H-NMR Spectroscopy (D<sub>2</sub>O, 500 MHz):  $\delta$  (ppm) = 8.2 - 7.0 (15H, br, Pyr), 4.6 - 2.8 (455H, br, cellulose backbone). FT-IR (ATR) = 3376, 2875, 1646, 1564, 1354, 1054, 887 cm<sup>-1</sup>. GPC (H<sub>2</sub>O): M<sub>n</sub> (PDI) = 1.07 x 10<sup>6</sup> g mol<sup>-1</sup> (1.1).

## Synthesis of styrene methyl viologen monomer (St-MV)

Synthesis was carried out according to previously published protocol.<sup>4</sup> Monomethyl bipyridine (1.21 g, 4.06 mmol) and 4-vinylbenzyl chloride (0.69 g, 0.63 ml, 4.5 mmol) were dissolved in acetonitrile (MeCN, 40 mL) and bubbled with nitrogen before heating to 60°C overnight. The mixture was allowed to cool and the solid isolated by filtration to yield a red solid (1.16 g, 2.57 mmol, 63%). <sup>1</sup>H-NMR Spectroscopy (D<sub>2</sub>O, 400 MHz):  $\delta$  (ppm) = 9.1 (d, 2H), 8.9 (d, 2H), 8.5 (d, 2H), 8.4 (d, 2H), 7.6 (d, 2H), 7.4 (d, 2H), 6.8 (dd, 1H), 5.9 (d, 1H), 5.9 (s, 2H), 5.34 (d, 1H), 4.4 (s, 3H).

## Synthesis of PSt-MV

PSt-MV was synthesised according to previously published protocols.<sup>5</sup> 4-Vinylbenzyl(trimethylammonium) chloride (4.65 g, 22.00 mmol), StMV (1.1 g, 2.44 mmol) and 4,4'-azobis(4-cyanovaleric acid) (ACVA, 33.60 mg, 0.12 mmol) were dissolved in H<sub>2</sub>O:EtOH (1:1 by volume to make a total of 32 mL). The solution was then bubbled with nitrogen for 30 min and then heated to 70°C for 48 h. The polymer was then precipitated in diethyl ether and tetrahydrofuran (THF) before freeze drying from aqueous solution to yield an orange solid (3.57 g). <sup>1</sup>H-NMR Spectroscopy (D<sub>2</sub>O, 400 MHz):  $\delta$  (ppm) = 9.01 (m, viologen), 8.48 (m, viologen), 7.21 (m, styrene), 6.6 (m), 4.37 (m),

2.91 - 0.80 (polymer back bone). GPC (H<sub>2</sub>O): Mn (PDI) = 37.1 kDa (2.42).

## General preparation of supramolecular polymer networks

The molar ratio of Np and MV to CB[8] in each sample is always 1:1:1, unless stated otherwise. The general preparation method was constant for all samples. For example, HEC1300\*5Np (5 mg) was dissolved in water (0.5 mL) with mild heating and vortexing. PSt-MV (1.5 mg) and CB[8] (1 mg) were dissolved in water (0.5 mL) separately, heated and stirred. Both solutions were then mixed, heated and shaken to obtain pinkish, transparent polymer network.

## Time-Temperature Superposition (TTS) Principle

The shift factors can be correlated with the temperature by the Arrhenius equation as follows:

$$\log(a_{T_{ref}}) = \frac{E_a}{2.303R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (1)$$

where  $E_a$  is the activation energy in kJ mol<sup>-1</sup> and R is the gas constant (8.314 J K<sup>-1</sup>mol<sup>-1</sup>). The shift factors can be fitted linearly on the inverse of temperature (1/T) scale. The activation energy is a measure of energy barrier that must be overcome to allow for the relaxation of the viscoelastic material.

## Infinite relaxation spectrum fitting

To delineate the complex relaxation behavior of the materials investigated in this study, the rheological data were fit to a model of infinite Maxwell elements using MATLAB's *lsqcurvefit* function to a two-mode log-normal distribution of relaxation times according to:

$$H(\tau) = A_1 \exp\left(-\frac{(\ln(\tau) - \ln(\tau_1))^2}{2\sigma_1^2}\right) + A_2 \exp\left(-\frac{(\ln(\tau) - \ln(\tau_2))^2}{2\sigma_2^2}\right) \quad (2)$$

This distribution can be obtained by solving for the sum of squares of the difference of experimental and model  $G'$  and  $G''$  data using the following equations:

$$G'(\omega) = \int_{-\infty}^{\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d\ln(\tau) \quad (3)$$

$$G''(\omega) = \int_{-\infty}^{\infty} H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d\ln(\tau) \quad (4)$$

This model assumes an infinite parallel arrangement of Maxwell elements, which include a compliance (capacitance) and a dashpot (resistance) element in series. Each of the Maxwell elements exhibits a unique relaxation time constant.

## Supporting Rheological and Other Results

Table S1: Characteristics of HEC-Np polymers.

Polymer	$M_n$ (kg mol <sup>-1</sup> )	Degree of polymerisation	Np mol%	Number of Np per HEC backbone
HEC90*5Np	90	198	5	10
HEC250*5Np	250	551	5	28
HEC1300*5Np	1300	2863	5	143

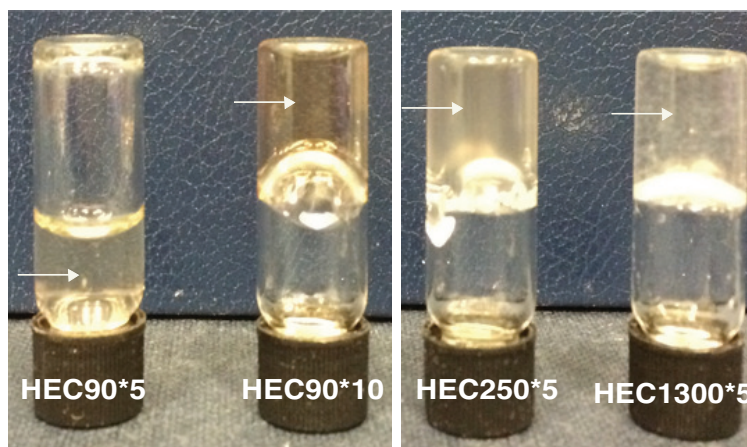


Figure S1: Inverted vial test for supramolecular polymer networks at 0.5 wt.% HEC-Np loading.

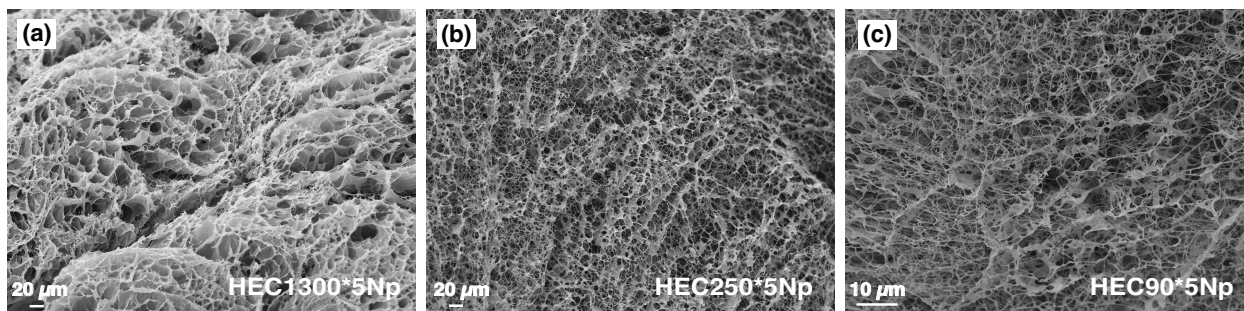


Figure S2: Scanning Electron Microscopy (SEM) images of supramolecular polymer networks with 0.5 wt.% HEC-Np loading using different MWs.

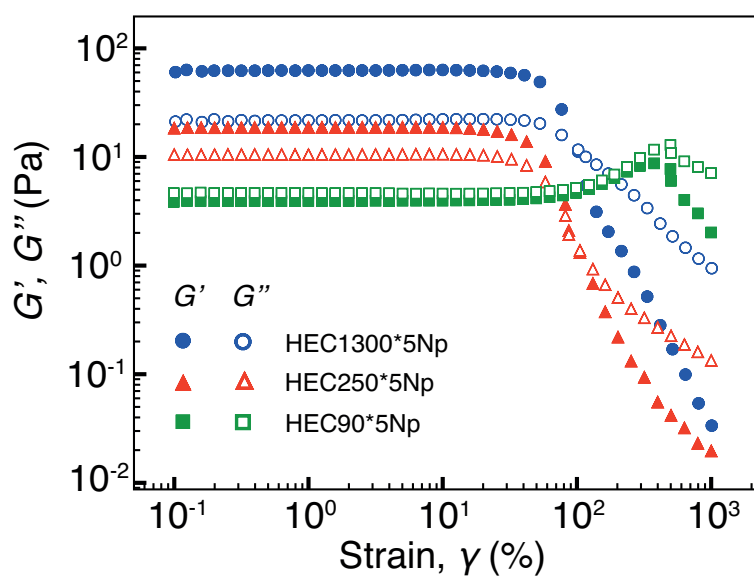


Figure S3: Storage and loss moduli from a strain amplitude sweep performed at  $10 \text{ rad s}^{-1}$  for different MW polymer networks.

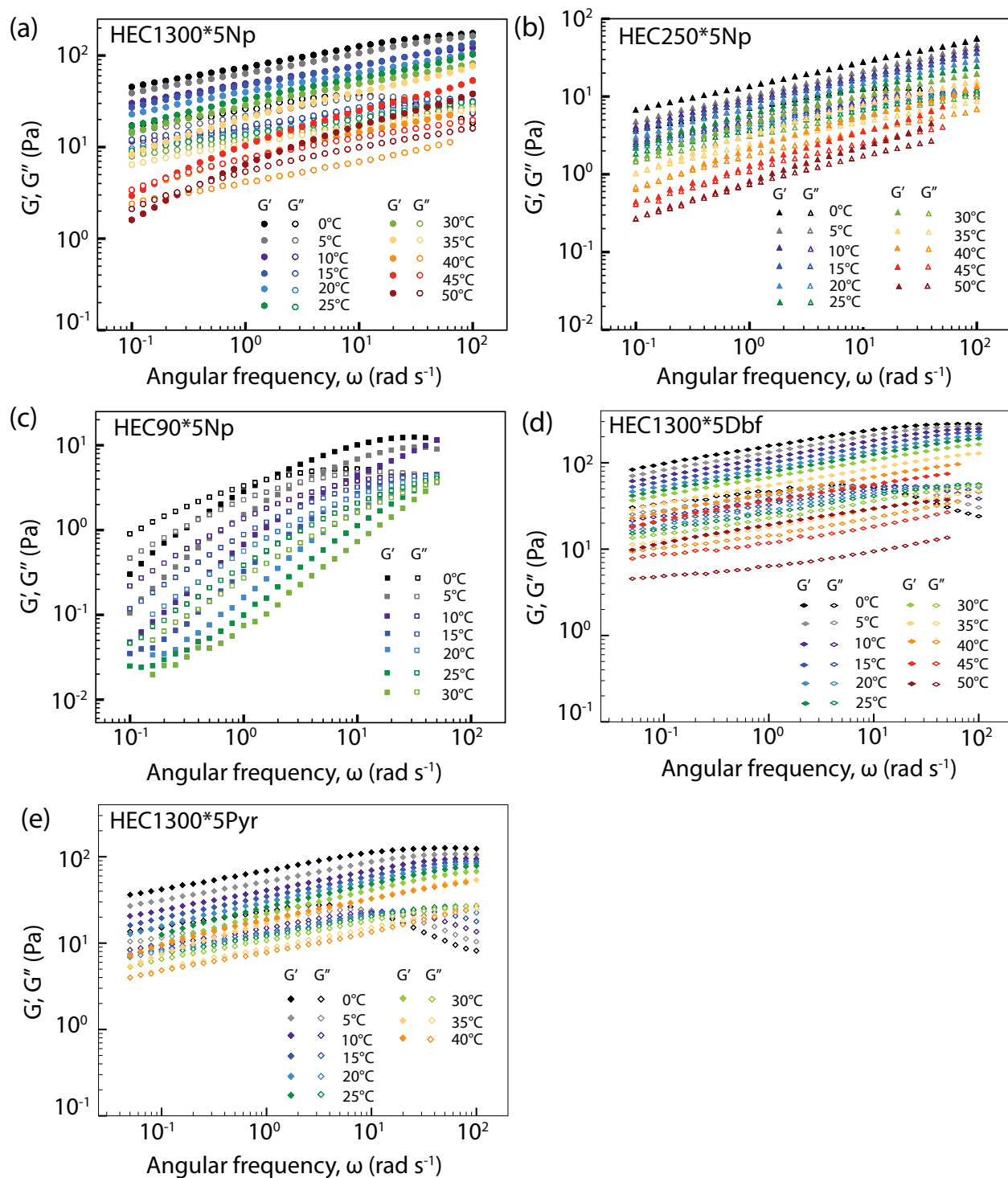


Figure S4: Temperature-dependent oscillatory frequency sweeps at 1% strain for all transient polymer networks with 0.5 wt.% HEC-G2 loading. These supramolecular polymer networks display thermoresponsiveness, exhibiting a solid-like behaviour at room temperature, while behaving liquid-like at elevated temperatures.



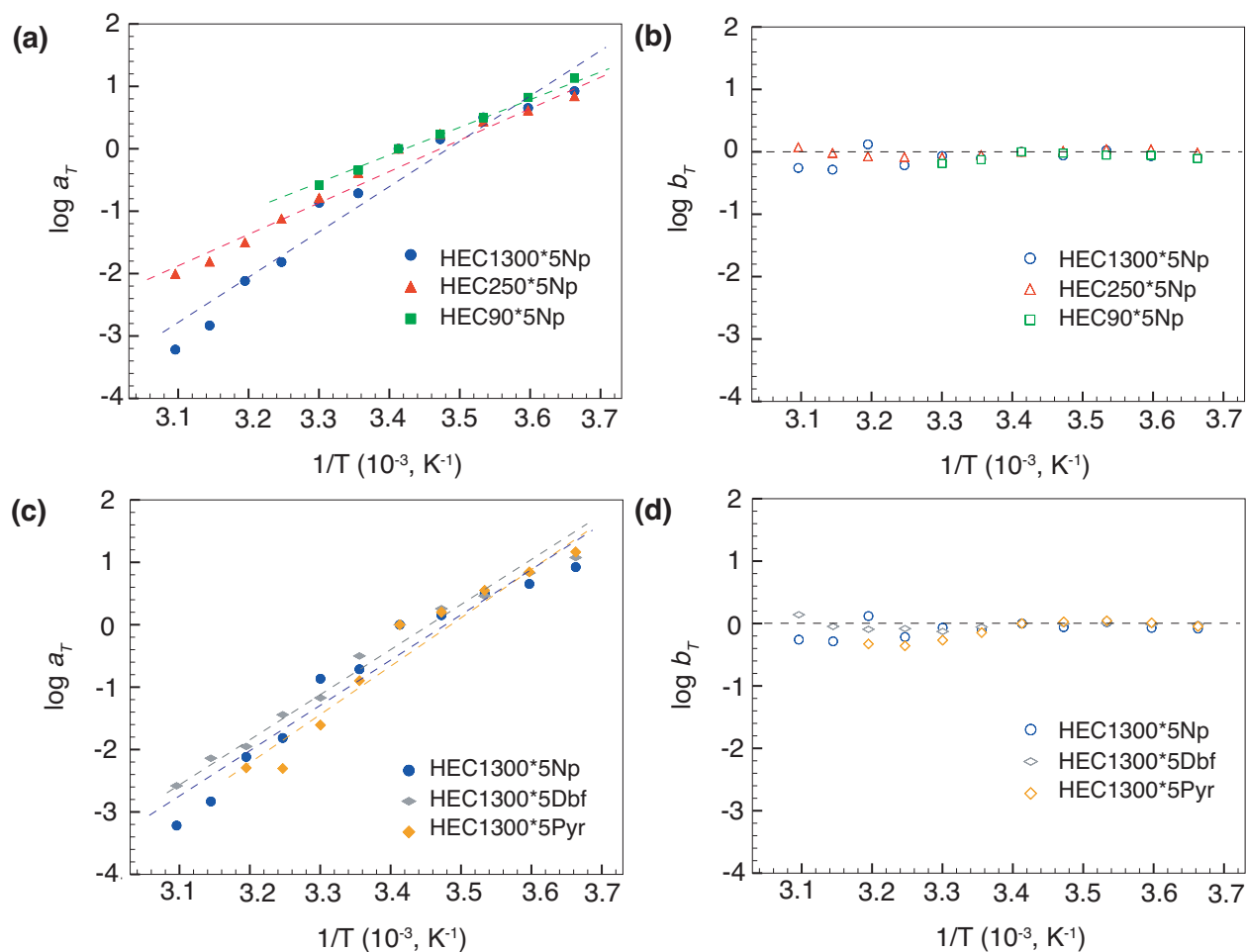


Figure S5: Temperature dependence of horizontal shift ( $a_T$ ) and vertical shift ( $b_T$ ) factors used in generating the master curves for supramolecular polymer networks using (a, b) different MW HEC-Np and (c, d) HEC1300 polymer functionalised with Np, Dbf and Pyr moieties. The apparent activation energy ( $E_a$ ) values were calculated from the slope of the curve. The  $E_a$  values were averaged across the temperature range of 0 - 50°C and found to be lower than the dissociation energy of covalent linkages (347  $\text{kJ mol}^{-1}$ ), demonstrating the dissociation of the ternary complexes is preferred upon deformation. The temperature dependence of the shift factor  $a_T$  shows that the activation energy of the Np-based polymer networks varies substantially over a wide range, 90 - 145  $\text{kJ mol}^{-1}$ , increasing as a function of the polymer molecular weight. In contrast, the activation energies for Dbf and Pyr ternary systems are 128 and 156  $\text{kJ mol}^{-1}$ , respectively, which do not differ significantly from that of the Np system consisting of similar polymer molecular weight. The variation in the results indicate a random distribution of guest molecules on the polymer backbones during the post-functionalisation of the polymers, leading to wide distribution of strength of host-guest association-dissociation at different temperatures.

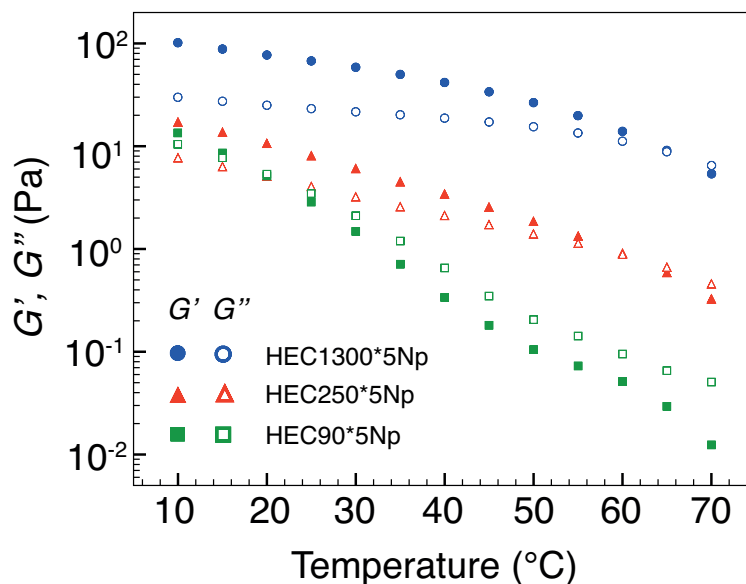


Figure S6: Dynamic moduli  $G'$  (closed symbols) and  $G''$  (open symbols) at  $10 \text{ rad s}^{-1}$  and heating/cooling rate of  $1 \text{ }^\circ\text{C min}^{-1}$  and a strain of 1% for supramolecular polymer networks with 0.5 wt.% HEC-Np loading. In the high MW networks (HEC1300\*5Np, HEC250\*5Np), a gel-like behaviour was still observed up to  $50^\circ\text{C}$ , in contrast to the low MW polymer networks which flowed readily above  $30^\circ\text{C}$ . Subsequent cooling from  $70$  to  $10^\circ\text{C}$  recovers most CB[8]-based crosslinks, and thus, their initial storage moduli.

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