# Controlling Spatiotemporal Mechanics of Supramolecular Hydrogel Networks with Highly Branched Cucurbit[8]uril Polyrotaxanes **

*Cindy Soo Yun Tan,* [a,b‡] *Ji Liu,* [a‡] *Alexander S. Groombridge,* [a] *Steven J. Barrow,* [a] *Cécile A. Dreiss,* [c] *Oren A. Scherman* [a]* *

Polymeric materials that incorporate dynamic interactions such as hydrogen bonding, host-guest molecular recognition and metal-ligand coordination, exhibit an array of intriguing properties, including shape memory, self-healing, adaptability and malleability.[1–9] Precisely-engineered materials with well-defined mechanical strength and processability are highly desirable for economically viable industrial uses.[8,10,11] Mechanical performance of such dynamic materials could be manually tuned through either spatial hierarchy (polymer architecture) or temporal hierarchy (crosslinking kinetics) for desirable strength and toughness.[10,12–16] Nevertheless, simultaneous control of chain dynamics and topological architecture of a polymer network remains elusive and is currently an area of intense scientific research.[10,17]

As one of the large member in cucurbit[$n$]uril macrocycles, CB[8] is capable of simultaneously accommodating an electron-deficient guest and another electron-rich guest.[18–20] The resulting 1:1:1 heteroternary supramolecular complexes can be utilised as a molecular binding motif, to dynamically hold two complementarily-functionalised units. We have recently reported a variety of supramolecular hydrogel networks exploiting suitable mixtures of guest-functionalized copolymers and CB[8] host molecules.[21–23] These hydrogels can be easily prepared from inexpensive renewable resources, exhibiting a high water content and superior biocompatibility. On account of their dynamic essence,

these CB[8]-based hydrogel networks exhibit remarkable shear-thinning and stress relaxation, thus can be readily injected through a medical syringe. Tremendous efforts have been devoted to manipulating CB[$n$] molecular recognition in a variety of hydrogel networks, in order to modulate their viscoelasticity and relaxation behaviors.[19,23,24] However, very few studies have been exclusively dedicated to the relationship between topological complexity, supramolecular dynamics and macroscopic mechanics until recently, which is the focus of our current study. Herein, we report a new class of supramolecular hydrogel networks assembled from a highly branched CB[8]-threaded polyrotaxane (HBP-CB[8]) and a linear naphthyl-functionalized hydroxyethyl cellulose (HECNp), as illustrated in **Figure 1**. The branched topology (spatial structure) generally affects polymer chain relaxation (temporal structure), and further dictates the toughness and other mechanics of a polymeric system.[12,13,17] From a macroscopic viewpoint, dynamic hydrogel networks consisted of highly-branched components may show remarkably different time- and temperature-dependent viscoelastic properties as well as thermal stability/reversibility, compared with that prepared from its linear analogues. The relationship between the macroscopic mechanics and spatiotemporal hierarchy as well as chain dynamics of the HBP-CB[8] supramolecular hydrogel networks was investigated.

A bisfunctional styrenic monomer containing a viologen derivative, St-MV$^{2+}$-St, was employed as a crosslinker to introduce branching points into a highly-branched polymer backbone. Viologen derivatives are typical first guests (electron-deficient) for CB[$n$] host molecules, with a binding constant ($K_a$) up to $10^6$ M$^{-1}$.[18] An aqueous solution of St-MV$^{2+}$-St and CB[$n$] ($n$ = 7 or 8) was continuously fed into a polymerisation system consisting of $N$-hydroxyethyl acrylamide (HEAm) as co-monomer, 4,4'-azobis(4-cyanovaleric acid) (ACVA) as initiator and benzyltrithiocarbonyl propionic acid (BCPA) as chain transfer agent (CTA), through a semi-batch reversible addition-fragmentation chain transfer (RAFT) polymerisation and cross-chain termination reactions[25] (**Figure 1a-i**, see *ESI Experimental Part* for details). In this case, gelation was substantially suppressed on account of a low St-MV$^{2+}$-St concentration, by maintaining a sufficiently high *in-situ* CTA/St-MV$^{2+}$-St ratio. HBP-CB[8], with a highly-branched chain topology and CB[8]

* [a] Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom.
E-mail: oas23@cam.ac.uk.
[b] Faculty of Applied Sciences, Universiti Teknologi MARA, 94300 Kota Samarahan, Sarawak, Malaysia.
[c] Institute of Pharmaceutical Science, King's College London, London SE1 9NH, United Kingdom.
‡ These authors contribute equally in this work.

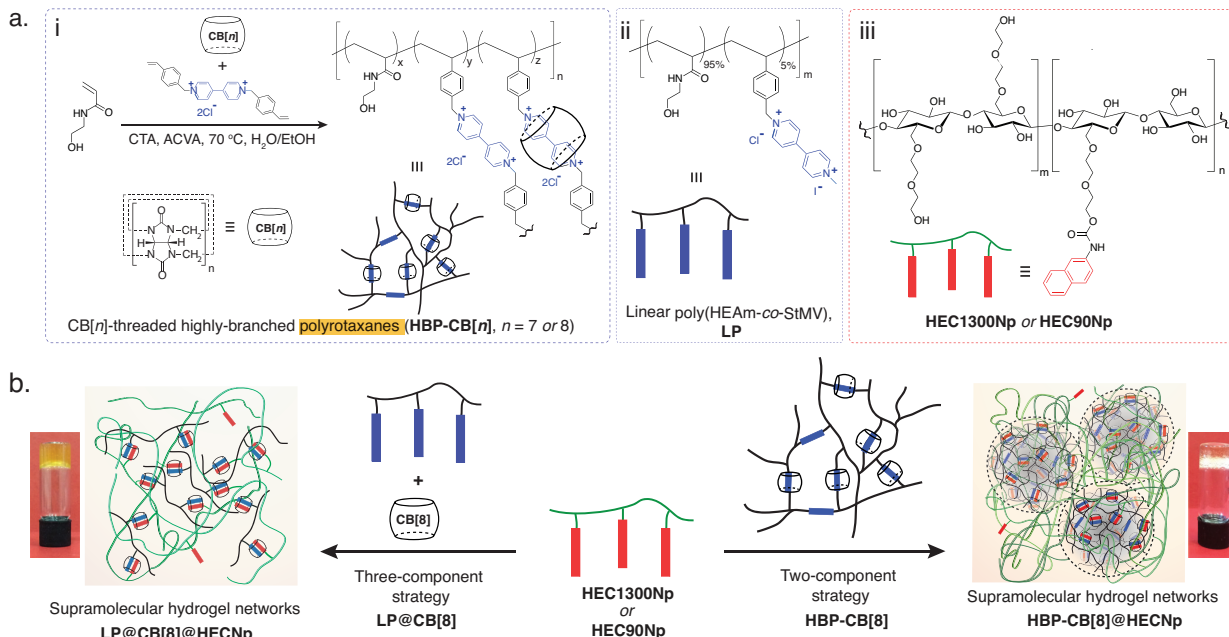Supporting information for this article is available on the WWW under or from the author.

**Figure 1. a.** Schematic illustration of: synthesis of the highly-branched CB[n]-threaded polyrotaxane (HBP-CB[n]) *via* a semi-batch RAFT polymerisation in the presence of CB[n] (i), chemical structures of its linear analogue (LP, ii) and naphthyl-functionalised hydroxyethyl cellulose (HECNp, iii). **b.** Formation of hydrogel networks through a *two-component strategy* from HBP-CB[8] polyrotaxane (HBP-CB[8]@HEC), or a *three-component strategy* from its linear analogue (LP@CB[8]@HEC). Inset: inverted vial tests for the hydrogel networks.

mechanically-locked within the polymer backbones, was obtained with a $M_w$ value of $(3.0 \pm 1.5) \times 10^6$ g mol$^{-1}$. Interestingly, the HBP-CB[8] could readily dissolve in water with a remarkably increased solubility of $C_{CB[8]}$ up to 20 mM, which is over $2000\times$ the solubility of pristine CB[8] ($< 10$ $\mu$M),[18] on account of the highly-hydrophilicity of polyHEAm backbones. This substantial increase in CB[8] solubility effectively overcomes many inherent limitations that have previously plagued CB[8]-based polymeric assemblies. Moreover, such a branched topology arising from the semi-batch RAFT polymerisation can readily be extended to other CB[n] homologues, such as CB[7], yielding a highly-branched CB[7]-threaded polyrotaxane (HBP-CB[7]). Since a second guest cannot further bind with a CB[7]·MV$^{2+}$ binary complex, HBP-CB[7] was further used as a control in the following investigation. Moreover, a linear analogue (LP), poly(HEAm-*co*-StMV), of similar composition was prepared using a mono-functional viologen-monomer (St-MV$^{2+}$) without CB[8] (**Figure 1a-ii**).

Self-assembly of two complementary guest-functionalised polymers, together with CB[8], has been used to construct a vast array of transient polymeric materials, by exploiting the CB[8] host-guest ternary complexation.[19,20] Most of the previously-reported CB[n] hydrogel networks employ a *three-component strategy* by mixing to guest-pedant polymers and CB[8] host molecules. Hydrogel networks with moderate viscoelastic properties were obtained,[21,22] on account of limited CB[8] solubility, and thus a limited degree of physical crosslinking, as well as high vis-

cosity of guest-functionalized polymer precursor solutions, leaving limited tuning of their macroscopic mechanics. Mechanically locking CB[n] onto HBP-CB[n] polymer backbones simplifies the preparation procedure from *three components* to *two components*, and remarkably increased the CB[8] solubility. Herein, naphthyl-functionalised HEC with $M_w$ of 1300 kDa (HEC1300Np) and 90 kDa (HEC90Np), and also a Np functionalisation degree of 5 *mol.%*, were used (**Figure 1a-iii**). Mixture of HBP-CB[8] and HEC1300Np (overall solid fraction of 2 *wt.%*) leads to the immediate formation of a transparent hydrogel network (HBP-CB[8]@HEC1300Np, **Figure 1b**). For comparison, the MV$^{2+}$-containing linear copolymer (LP), analogous to HBP-CB[8], was mixed with both HEC1300Np and CB[8] at equimolar host-guest ratio through a *three-component* process, yielding a bright yellow yet weak hydrogel network (LP@CB[8]@HEC1300Np, **Figure 1b**).

A broader linear viscoelastic region was observed for the HBP-CB[8]@HEC1300Np network (green dots) at 20 °C, compared to that of LP@CB[8]@HEC1300Np analogue (red dots) (**Figure 2a**). Slight strain hardening was detected for HBP-CB[8]@HEC1300Np network, which is not commonly observed for hydrogel networks from linear polymers, however, widely reported during the uniaxial extension of low molecular weight self-assemblies.[26] This strain hardening phenomena can be interpreted by the effect of chain overstretching and/or a strain-induced transformation from intrachain to interchain crosslinking, due to the presence of branched polymer backbones.[13,26,27]
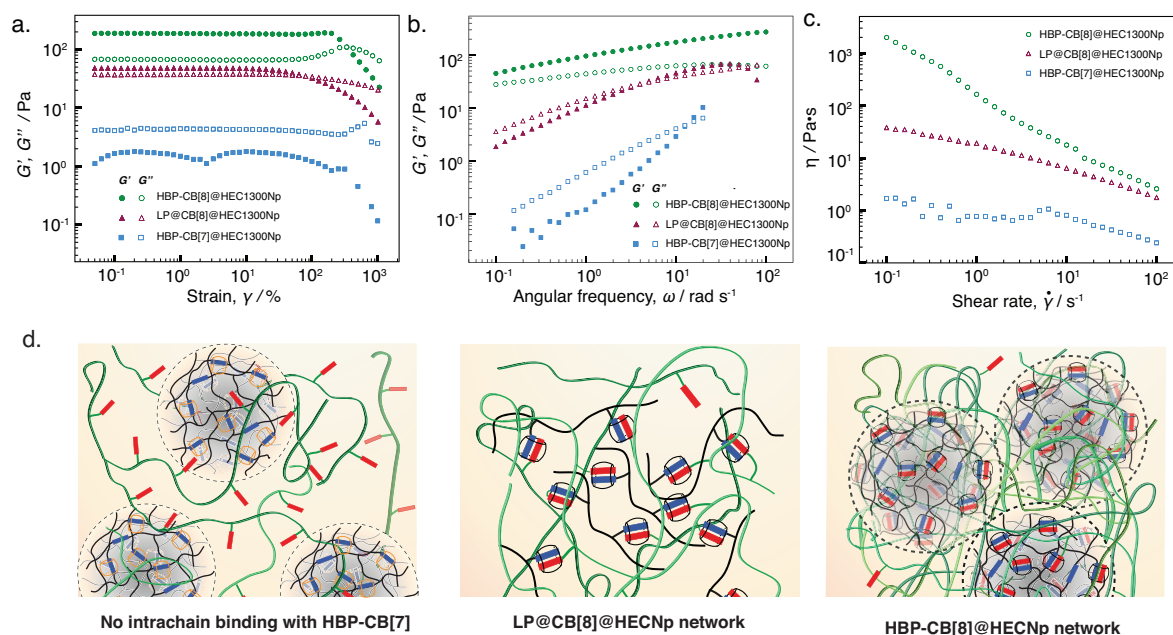
**Figure 2.** Rheological measurement of supramolecular CB[$n$]-based hydrogel networks (2 $wt$.%) made of naphthyl-functionalised HEC with highly branched CB[8]-threaded polyrotaxanes (HBP-CB[8]@HEC1300Np) or its linear analogue (LP@CB[8]@HEC1300Np), or CB[7]-threaded polyrotaxanes (HBP-CB[7]@HEC1300Np as a control): **a.** amplitude sweeps ($\omega$ at 10 rad s$^{-1}$, $\gamma$ from 0.05 to 1000%), **b.** frequency sweeps ($\gamma$ at 1%, $\omega$ from 0.1 to 100 rad s$^{-1}$), and **c.** steady-state shear sweeps (0.1 to 100 s$^{-1}$). **d.** Schematic illustration of the supramolecular CB[$n$] networks: dotted grey areas represent the globular topology of the highly branched polyrotaxanes; HBP-CB[7] was employed as a control since no ternary complexes form within the CB[7] cavity.

In the frequency sweeps of HBP-CB[8]@HEC1300Np hydrogel network (**Figure 2b**), the elastic modulus ($G'$) is higher than loss modulus ($G''$) over the whole range of frequencies measured, while both $G'$ and $G''$ are relatively independent of frequency. In contrast, the LP@CB[8]@HEC1300Np network behaves like a viscoelastic liquid with much lower moduli, and a crossover between $G'$ and $G''$ at an intermediate angular frequency (between 1 and 10 rad s$^{-1}$). In the steady-state measurements (**Figure 2c**), both HBP-CB[8]@HEC1300Np and LP@CB[8]@HEC1300Np networks exhibit shear-thinning behaviour. Moreover, the branched system exhibits a higher dependence on shear rate, and also a higher viscosity at low shear rates (*ca.* 2000 Pa·s at 0.1 $s^{-1}$) was observed, compared to 100 Pa·s for its linear analogue. The lower viscosity and magnitude of both $G'$ and $G''$ for LP@CB[8]@HEC1300Np network reflects fewer entanglements and a lower number of effective crosslinks presenting in the LP network. Another control sample HBP-CB[7]@HEC1300Np shows liquid-like behavior with low viscoelastic moduli (**Figure 2a-b**), since the smaller cavity of CB[7] cannot afford any supramolecular crosslinks. On account of the extremely low viscosity of HBP-CB[7]@HEC1300Np, inertia effects at higher angular frequencies were observed, and thus data beyond the $G'$ - $G''$ crossover point are not shown in **Figure 2b**. A Newtonian response with very low viscosity in steady-state measurement indicates the absence of an interconnected network (**Fig-ure 2c**). Schematic representations of all the supramolecular network systems described above are shown in **Figure 2d**, where the presence of a branched topology in the HBP-CB[8] polyrotaxanes promotes the formation of highly crosslinked networks *via* dynamic host-guest interactions, thus enhancing mechanical and flow performance.

In order to evaluate the effect of branching topology on the chain dynamics, thermal stability and reversibility, cyclic temperature-sweep rheological measurements were carried out. As shown in **Figure 3a**, the highly interconnected HBP-CB[8]@HEC1300Np network could maintain its integrity up to 50 °C, after which point $G'$ began to drop below $G''$. Its modulus fully recovered upon subsequent cooling, indicating an excellent thermal stability and reversibility of mechanical performance. On the contrary, the LP@CB[8]@HEC1300Np network was completely destroyed upon heating, and readily flowed at 40 °C (see **ESI, Figure S3**). Moreover, modulus recovery was inconsistent as the temperature gradually decreased from 60 °C, indicating major local restructuring of the network. It is important to note that the HBP-CB[8]@HEC1300Np network does not undergo a phase separation over a wide temperature range, as opposed to other linear/branched polymer mixtures in which phase separation was detected during heating.[28] Therefore, combination of the highly branched topology and dynamic host-guest interactions remarkably improves the thermal stability, as well as the reversiblity of these supramolecular hydrogel networks.
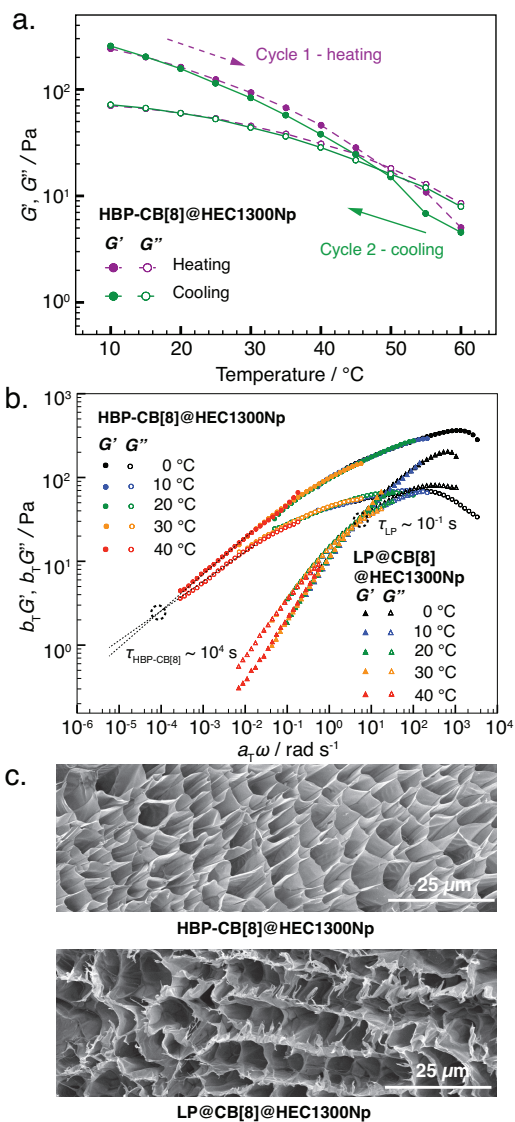
**a.** 

**b.** 

**c.** 

**HBP-CB[8]@HEC1300Np**



**LP@CB[8]@HEC1300Np**

**Figure 3. a.** Evolution of $G'$ and $G''$ for HBP-CB[8]@HEC1300Np sample (2 *wt.%*) during a cyclic heating and cooling process ($\gamma$ at 1%, $\omega$ at 10 rad s$^{-1}$). **b.** TTS master curves (referenced at 20 °C) and **c.** SEM images of the HBP-CB[8]@HEC1300Np and LP@CB[8]@HEC1300Np hydrogel networks.

Self-healing capability of the HBP-CB[8]@HEC1300Np hydrogel networks was measured in rheological step-strain measurements (at 20 °C), where a large-amplitude sweep ($\gamma$ = 1000%, $\omega$ = 10 rad s$^{-1}$) induced destruction of the 3D network structures ($G' < G''$). Complete recovery of the network's viscoelasticity was detected in a matter of seconds, during the subsequent small-amplitude sweeps ($\gamma$ = 0.05%, $\omega$ = 10 rad s$^{-1}$). Furthermore, rapid self-healing was detected over many cycles (see **ESI, Figure S4a**), arising from the fast CB[8] host-guest association kinetics. In step-shear measurements at 50 °C (see **ESI Figure S4b**), structural and thermal stability of the HBP-CB[8]@HEC1300Np network is further confirmed by consistent recovery of the initial viscosity over three cycles, corroborating a higher-density local crosslinks compared to its LP analogue. Although the LP@CB[8]@HEC1300Np system can self heal over a short period of time, it appears to be more 'mobile' and thus, more susceptible to thermodynamical structural reorganisation, compared with the heavily-intertwined and highly-branched HBP-CB[8]@HEC1300Np network.

Temperature-dependent viscoelastic properties of both HBP-CB[8]@HEC1300Np and LP@CB[8]@HEC1300Np hydrogel networks were investigated to differentiate their characteristic relaxation time ($\tau_c = 1/\omega_c$, where $\omega_c$ is the crossover angular frequency of $G'$ and $G''$). $\tau_c$ can be taken as the time scale needed for the dissociation or exchange of crosslinking, in order to relax the stress within the networks.[12] By following the time-temperature superposition (TTS) principle, a rheological master curve for each network was plotted from oscillatory frequency sweeps referenced at 20 °C (**Figure 3b**). Relaxation of the LP@CB[8]@HEC1300Np network occurred at $\omega_c \sim 10$ rad s$^{-1}$, indicating a fast relaxation mode ($\tau_c \sim 10^{-1}$ s), triggered by the synergistic dissociation of several crosslinking motifs, as well as subsequent chain reptation. In contrast, the HBP-CB[8]@HEC1300Np assembly showed a much longer time scale with $\tau \sim$ upto $10^4$ s. This can be attributed to the highly branched architecture and a hierarchical relaxation process of these dynamically bound polymer clusters (**Figure 2d**), which starts from the relaxation of shorter branches, followed by the whole chain backbone.[29]

To further probe the versatility of spatiotemporal control over mechanical properties of CB[8] hydrogel networks, we further extended this *two-component strategy* to polymer backbones with a lower molecular weight, for example HEC90Np (90 kDa, 5 *mol.%* Np). Surprisingly, a sol-gel transition was detected for the HBP-CB[8]@HEC90Np system (solid fraction of 2 *wt.%*), while the mixture with the linear analogue only yielded a flowing fluid (**Figure 4a** and **ESI Figure S7**). Compared with the HBP-CB[8]@HEC1300Np, the hydrogel network made of HEC90Np exhibited a significantly shorter relaxation time ($\tau_c \sim 10^1$ s, **Figure 4b**), due to the notably decreased chain entanglement; however, it still behaved as a viscoelastic network within the experimental timescales (**Figure 4a**). Plotting of $\ln(a_T)$ versus $1/T$ (inset in **ESI Figure S9**) follows a linear tendency over the range of temperatures studied, demonstrating that the viscoelasticity of all hydrogel networks exhibit an Arrhenius behaviour. Activation energy ($E_a$), estimated from plotting the empirical horizontal shift ($a_T$) as a function of temperature, was in the range of 145–165 kJ mol$^{-1}$ for the highly-branched systems (HBP-CB[8]@HEC1300Np and HBP-CB[8]@HEC90Np), while a much lower $E_a$ for the linear counterpart (LP@CB[8]@HEC1300Np, *ca.* 85 kJ mol$^{-1}$, see **ESI, Figure S9**) was estimated, in agreement with other highly-branched systems.[30] During the SEM observation, well-defined interconnected pores were detected for the HBP-CB[8] hydrogel networks (**Figure 3c** and **ESI, Figure S10**), while irregular pores with rough edges were detected for LP@CB[8]@HEC1300Np analogue (**Figure 3c**).
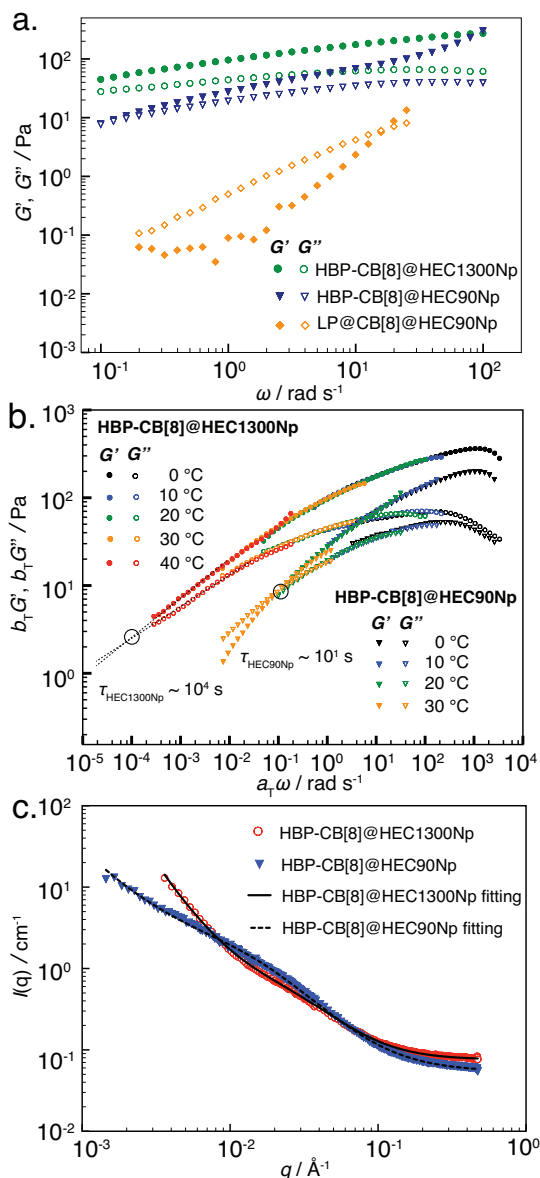
**Figure 4.** HPB-CB[8]-based hydrogel network made from low-molecular-weight HEC90Np (HBP-CB[8]@HEC90Np, 2 *wt.%*), compared to its linear analogue LP@CB[8]@HEC90Np and high molecular weight HBP-CB[8]@HEC1300Np: **a.** frequency sweeps ($\gamma$ at 1%, $\omega$ from 0.1 to 100 rad s$^{-1}$), **b.** TTS master curves referenced at 20 °C, and **c.** SANS measurements in D$_2$O.

SANS measurements of the HBP-CB[8] and hydrogel networks made of HBP-CB[8] with HEC90Np or HEC1300Np (**Figure 4c**) were conducted using the D33 instrument at the Institut Laue-Langevin (Grenoble, France). The scattering from HBP-CB[8] on its own was fitted with Equation 2 (see *ESI Experimental Section* for details), taking into account the presence of a broad peak in the scattering curve, yielding an exponent $n = 1.67$ for the Lorentzian

(characteristic of highly swollen chains in a good solvent), and a correlation length ($\xi$) of 38 Å with a characteristic distance ($d$) $\sim$ 300 Å ($d = 2\pi/q_0$). This model reflects a hierarchical organisation within the highly-branched polymer backbones. SANS curves of the hydrogel network samples were fitted with the Ornstein Zerniche model combined to a Porod law to account for large aggregates detected at low $q$ (see *ESI Experimental Section* for details, Equation 1, $n = 2$), giving $\xi$ of 67 and 36 Å for the HBP-CB[8]@HEC90Np and HBP-CB[8]@HEC1300Np, respectively. All these indicate a denser network for the hydrogel formed with the larger molecular weight HEC1300Np than that of HEC90Np, in agreement with the mechanical studies and SEM observation.

We have demonstrated that by manipulating the spatial topology of a polymeric component the mechanical and flow properties, as well as the processability of the viscoelastic materials, could be readily tailored. Nevertheless, at an industrial scale, macroscopic polymer mechanics routinely rely on tuning on molecular weight, crosslinking degree and/or concentration. In this case, polymers with branched topology may be more attractive on account of an increase in interchain interactions and retarded chain mobility, enabling a higher degree of fine tuning of material behavior.[10,17] As such, these highly branched HBP-CB[8] polyrotaxanes are promising alternatives for linear polymers and dendrimers in myriad industrial applications, where structural perfection is not crucial, on account of their relatively similar properties and facile scalable preparation.

In summary, we have demonstrated a new class of CB[8]-based supramolecular hydrogel network, which offers a practical alternative to previously reported systems, by exploiting the use of highly-branched CB[8]-threaded polyrotaxanes, through a simplified two-component strategy. Compared with hydrogel networks consisting of linear analogues, the branched architecture and its dynamics appear to dominate the bulk viscoelastic material response, giving rise to superior viscoelastic modulus, thermal stability and self-repairing/healing performance. A branched topology in the HBP-CB[8] polymer clearly extends the characteristic relaxation time in a hierarchical manner, and thus their mechanical performance can be tailored over a broad range of time and length scales. Given the extensive choice of aromatic molecules that are known to bind with CB[8]·MV binary complexes as second guests, hydrogel networks based on HBP-CB[8] can be endowed with a broader scope of adaptive functionalities, such as pH, redox and light responsiveness, which are all facilitated by the supramolecular heteroternary complexation. It is anticipated that the inherent coupling of spatial and temporal hierarchical control over macroscopic mechanics of a polymeric network offers exciting opportunities in engineering of functional supramolecular materials.

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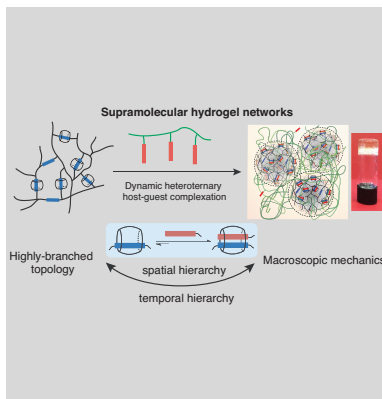
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**Supramolecular Hydrogel Networks**

*Cindy Soo Yun Tan, [a,b‡] Ji Liu, [a‡] Alexander S. Groombridge, [a] Steven J. Barrow, [a] Cécile A. Dreiss, [c] Oren A. Scherman [a]\**

**Controlling Spatiotemporal Mechanics of Supramolecular Hydrogel Networks with Highly Branched Cucurbit[8]uril Polyrotaxanes**



Formation of hydrogel networks through a *two-component* strategy from highly-branched CB[8]-threaded polyrotaxanes, exploiting the dynamic CB[8]-based heteroternary host-guest complexation. The branched architecture enables tuning of the hydrogel network dynamics *via* both topological (spatial hierarchy) and kinetic (temporal hierarchy) control.

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