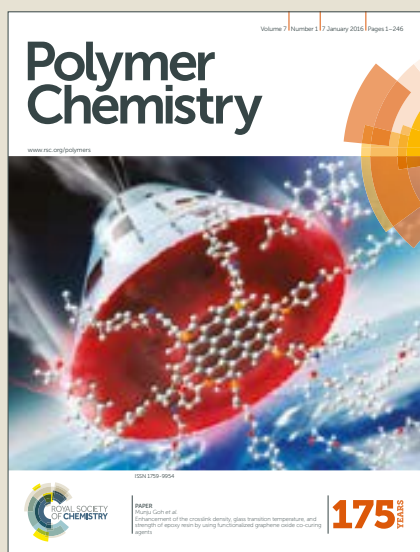


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Distinguishing Relaxation Dynamics in Transiently Crosslinked Polymeric Networks[†]

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Polymeric materials based on reversible non-covalent associations possess diverse mechanical behaviour, responsiveness to external stimuli and self-healing properties. Unlike covalently-bonded polymeric materials, whose properties are conventionally engineered through the polymer structure alone, the mechanical performance of a supramolecular material can be designed *via* two motifs: the polymer architecture (*e.g.*, polymer molecular weight or structure) and the physical crosslinks (*e.g.*, thermodynamics or kinetics of binding) between polymers. Here, we demonstrate the preparation of aqueous-based supramolecular polymeric materials utilising cucurbit[8]uril (CB[8]) crosslinking of multivalent polymers of varying molecular weights. By exploiting three kinetically distinct supramolecular motifs, we show that it is possible to relate the contributions of polymer architecture and dynamic crosslinking to the ultimate mechanical properties of the materials. These studies improve our understanding of the challenging relationships between design of supramolecular polymeric materials and their complex viscoelastic behaviour as well as relaxation dynamics.

1 Introduction

Macroscopic mechanical properties of supramolecular crosslinked polymeric materials can be engineered *via* two dimensions: macromolecular architecture and the supramolecular motifs involved in crosslinking. These soft materials typically possess structural motifs operating at characteristic hierarchical length and time scales, with dynamic interactions having been identified as the most critical in engineering tough supramolecular polymer networks and hydrogels.^{1–7} Although the mechanical response of the dynamic network is directly impacted by supramolecular crosslinking,^{8,9} the contribution of conventional polymer dynamics (such as polymer molecular weight and architecture) must also be considered to more fully understand the fundamental behaviour of these materials and to broaden the scope of their applicability.¹⁰ Yet, the polymer dynamics is often inherently coupled with the temporal kinetics of soft materials on account of diffu-

sion of the transiently connected polymeric constituents.¹¹

The lifetime of a transient crosslink plays a central role in defining the physical characteristics of supramolecular networks,¹² clearly distinguishing these materials from either their covalently crosslinked counterparts or entangled polymer solutions. Most supramolecular polymer networks exhibit remarkable viscoelastic behaviour, including long relaxation times (slower diffusion) and increased storage modulus in the rubbery region through connectivity of the network.¹³ Numerous efforts have been directed towards unravelling the complex equilibrium and dynamic properties of various reversible crosslinking motifs in polymeric assemblies,^{13–18} with more recent work investigating metal coordination^{19–22} and hydrogen bonded^{23–25} constructs. Holten-Andersen and coworkers reported on the mechanical performance of poly(ethylene glycol) (PEG)-based hydrogels crosslinked with multiple, kinetically distinct and dynamic metal-ligand coordination complexes simultaneously to orthogonally control the temporal hierarchy.¹¹ Nevertheless, few reports have simultaneously probed both the molecular kinetics and polymer dynamics of physically crosslinked networks. Recently, Guan *et al.* reported the preparation of copolymers containing imidazole ligands, which could be crosslinked through coordination to various metal ions, allowing the authors to engineer the mechanical responses of the network *via* ligand exchange-induced relaxation (temporal) as well as coordination geometry and topology (structural) under dynamic and static loading.¹⁹ The authors observed

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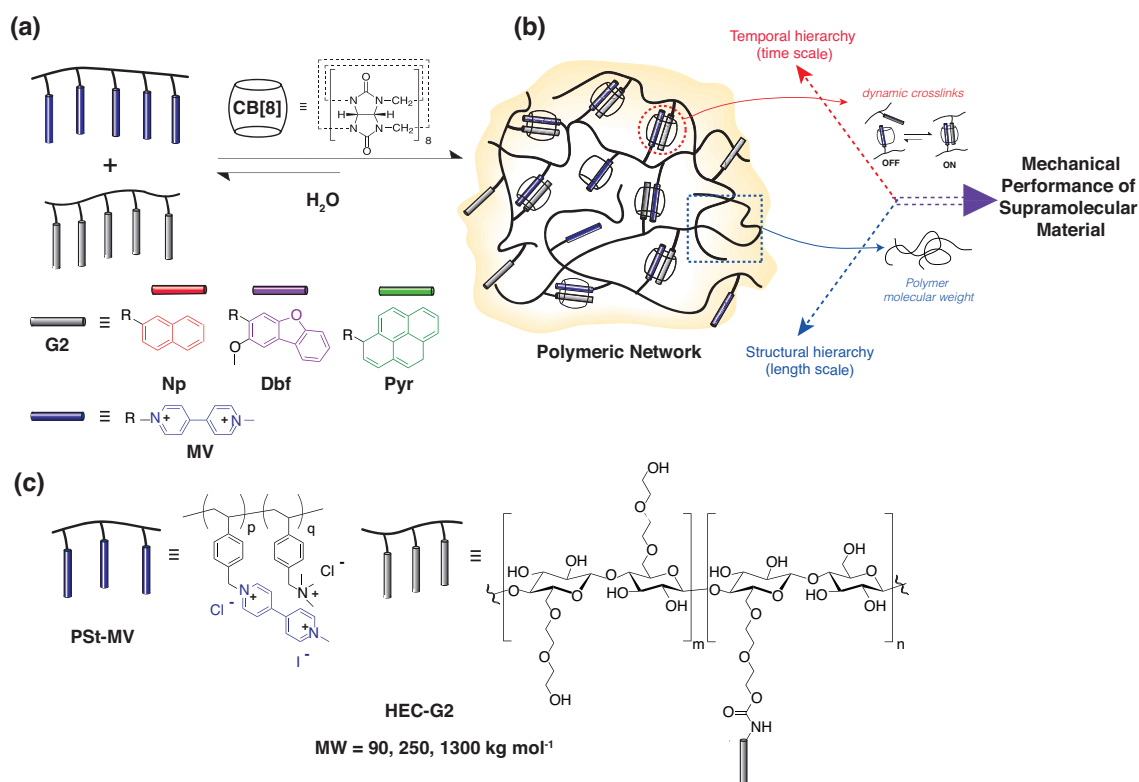


Fig. 1 (a) Schematic representation of supramolecular polymer network formation, whereby multivalent side-chain-functional polymers containing viologen and second-guest (G2; naphthyl - Np, dibenzofuranyl - Dbf, and pyrenyl - Pyr) derivatives are dynamically crosslinked by cucurbit[8]uril (CB[8]) to form heteroternary complexes. (b) Orthogonal structural and temporal controls of material mechanical performance: alteration of the polymer molecular weight can tune the viscoelastic properties of a transient polymer network in a conventional manner. Meanwhile, controlling the temporal CB[8] crosslinking dynamics by varying the type of second guest allows orthogonal control over its polymer dynamics by incorporating different second guests to bind with CB[8]·MV complex in the polymer networks. (c) Model molecular structures employed in the preparation of CB[8]-based physical polymer networks.

that while strong metal-ligand complexation resulted in mechanical behaviour similar to that of covalently crosslinked networks, weaker complexation afforded tunable temporal control over the mechanical properties and stress-dissipation. Inspired by the approaches taken in these previous studies, as well as their shortcomings, we sought to exploit a system of kinetically distinct host-guest interactions to dynamically crosslink multivalent polymers of varying molecular weights, thus affording complete decoupling of the relative contributions of dynamic crosslinking and classical polymer properties to the complex mechanical behaviour of these materials. These studies dramatically improve our understanding of the challenging relationships between the hierarchical construction and resulting complex viscoelastic mechanical behaviour of these materials, which can inform the design of more advanced supramolecular polymeric materials.

2 Results and Discussion

Here we develop a platform of supramolecular crosslinked networks consisting of disparate guest-functionalised polymers with differing polymer mechanics brought together by host-guest ternary complexation.^{26–29} CB[8] host molecule has a large cavity and can simultaneously accommodate two guests in a

step binding process, whereby an electron-deficient first guest such as a viologen derivative (MV) enters first, followed by an electron-rich second guest, typically a polycyclic aromatic hydrocarbon, to form a stable 1:1:1 ternary complex.³⁰ These complexes exhibit exceptionally high equilibrium binding affinities (K_a up to 10^{14} M^{-2}).³¹ In our system, multivalent styrenic copolymers bearing MV derivatives can be dynamically crosslinked with hydroxyethylcellulose (HEC) polymers bearing a second guest moiety, consisting of either naphthyl (Np), dibenzofuranyl (Dbf) or pyrenyl (Pyr) derivatives, through the addition of CB[8] molecules (Figure 1a). We demonstrate independent control over the time-dependent mechanical properties of these CB[8]-mediated polymer networks from both polymer molecular weight and temporal properties (Figure 1b) to modulate the macroscopic time-dependent mechanical properties of the polymer network. The structural dimension of the polymer network is isolated from their temporal hierarchy systematically by using an identical second-guest crosslinking motif appended on different polymer backbones, allowing the material design to be orthogonally manipulated from both dimensions, exclusively. Likewise, we are also able to engineer the time-dependent mechanical properties through the choice of second guest moieties involved

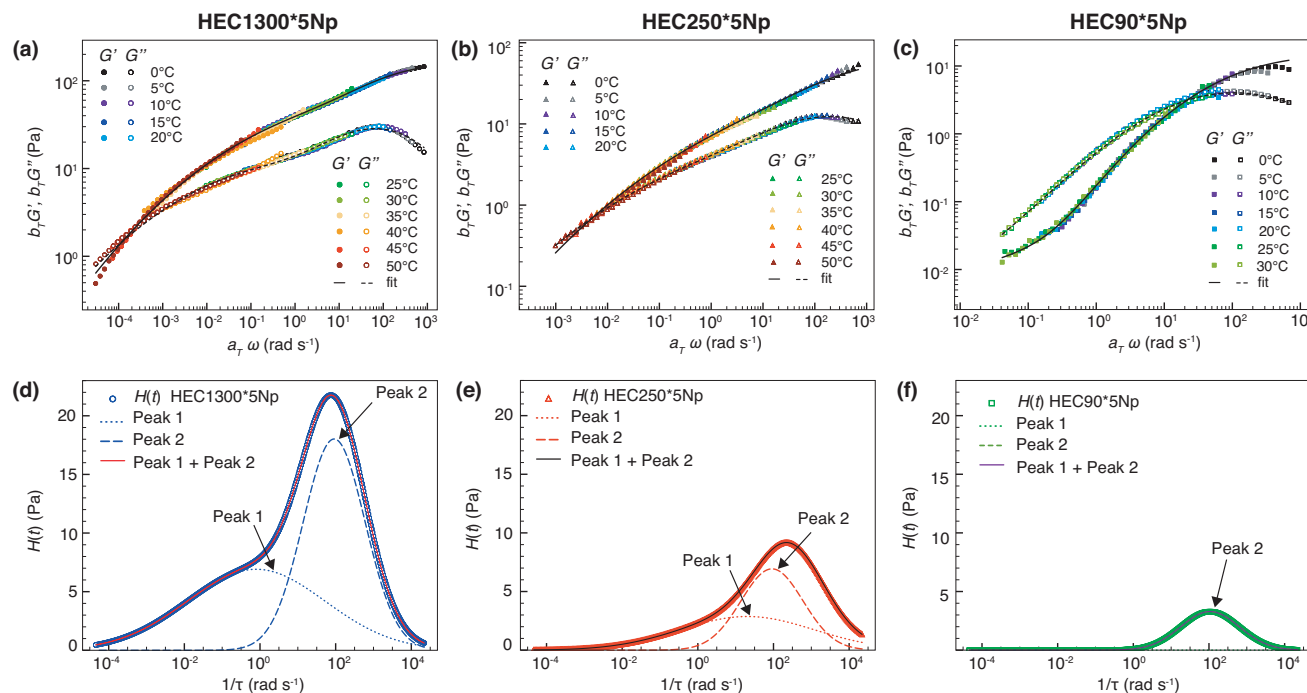


Fig. 2 Master curves of the viscoelastic moduli for (a) HEC1300*5Np, (b) HEC250*5Np, and (c) HEC90*5Np networks referenced to 20°C. Increasing the polymer molecular weight in the supramolecular networks downshifts the G' and G'' crossover frequency (τ_c) by several orders of magnitude. The polymer networks are well-characterised by relaxation spectra $H(\tau)$ with one or two local maxima, denoted as Peak 1 and Peak 2. The deconvoluted peaks represent stress dissipation in the polymer network attributable to dissociation of $\text{CB}[8] \cdot \text{MV} \cdot \text{Np}$ at high ω and molecular weight dependent peaks shifting towards lower ω (d - f). The top figures (a - c) compare the experimental G' and G'' data of the networks superimposed with the best-fit lines of G' and G'' generated from fitting a two-mode relaxation spectrum, $H(\tau)$, in the bottom figures (d - f).

in the $\text{CB}[8]$ crosslinking.

2.1 Determination of the contribution of polymer molecular weight to mechanical performance

We first sought to investigate the role of polymer molecular weight on the dynamic mechanical behaviour of transient networks based on $\text{CB}[8] \cdot \text{MV} \cdot \text{Np}$ ternary binding. In a random polymer functionalisation, long polymer chains carry higher number of stickers than short chains.³² Hence, by adjusting the molecular weight of the polymer, the number of crosslinks per chain can be tuned (See **Table S1**) while keeping the degree of crosslinking in the network constant. A series of HECs with different molecular weights ($\text{MW} = 90, 250, \text{ and } 1300 \text{ kg mol}^{-1}$) were functionalised with Np moieties using isocyanate coupling chemistry,³³ each containing the same molar loading of Np moieties (5 mol% Np), as shown in **Table S1**. These HEC-Np polymers were named according to their MW and Np loading accordingly: $\text{HEC}(\text{MW})^*(\text{fraction})\text{Np}$. The HEC-Np polymers were then mixed with an aqueous solution containing $\text{CB}[8]$ and viologen-containing styrenic copolymer (PSt-MV), ensuring 1:1:1 ratio of $\text{CB}[8] \cdot \text{MV} \cdot \text{Np}$ to form supramolecular polymer networks (**Figure 1a** and **Figures S1** and **S2**). The HEC-Np concentration used in this study was maintained in the semi-dilute regime, between 0.2 and 1 wt.%.

Effects of molecular weight during the frequent breaking and

reformation of $\text{CB}[8] \cdot \text{MV} \cdot \text{Np}$ crosslinks can be decoupled by keeping the semi-dilute concentration of HEC-Np polymer below the critical concentration of entanglement, allowing us to independently modulate the network's multiple hierarchical timescales (**Figure 1b**). The Np "stickers" dissociate (known as the "OFF" state) on a characteristic timescale, allowing the polymers to diffuse before re-associating with another "sticker" (known as the "ON" state), as shown in **Figure 1b**. As a result, bulk mechanical properties and relaxation time of these semi-dilute cellulosic supramolecular polymer networks can then be tailored from their temporal kinetics. Dynamic polymer networks generally exhibit physical characteristics described in the "sticky Rouse" or "sticky reptation" models of associative polymer networks, however, these theories only work for simple transient systems.^{13,34,35}

Time-dependent mechanical properties for these polymeric networks were examined by small-amplitude oscillatory rheological measurements from 0 to 50°C. Storage (G') and loss (G'') moduli were measured as a function of angular frequency (ω) in the material's linear viscoelastic regime at 1% oscillating strain (**Figure S3**). Time-temperature superposition (TTS) was applied using the temperature dependent G' and G'' values. Master curves for G' and G'' versus reduced angular frequency (ω_{aT}) for $\text{CB}[8]$ -based polymer assemblies were constructed referenced at temperature of 20°C (**Figure 2**, **Figure S4**). For all molecular weights investigated in this study, the superposition of the viscoelastic

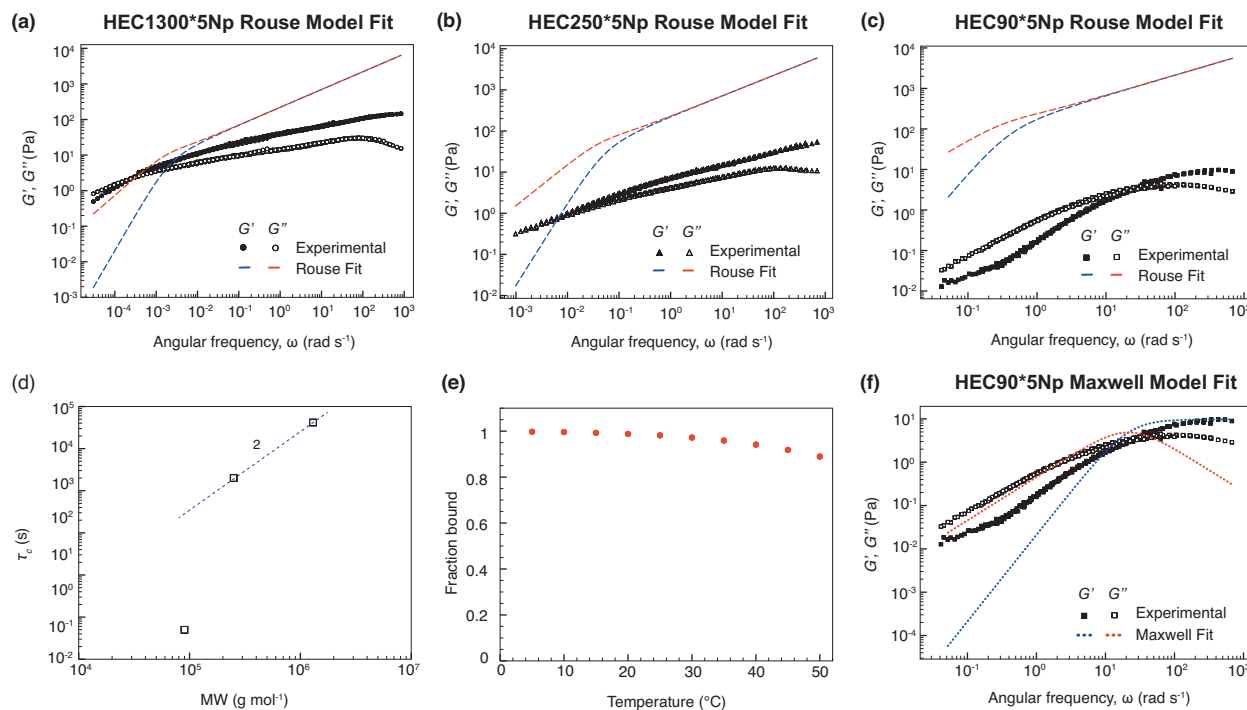


Fig. 3 Experimental G' and G'' data plotted alongside the corresponding sticky Rouse model for (a) HEC1300*5Np, (b) HEC250*5Np, and (c) HEC90*5Np demonstrates that this model is unable to adequately model the experimental data in any of these cases; (d) the longest relaxation time (τ_c) values scale linearly for higher molecular weight HEC-Np polymers when fitting a power law to the upper two out of three data, giving a scaling exponent of 2, which describes a Rouse-like scaling behaviour; (e) fraction of bound CB[8]·MV·Np ternary complexes with increasing temperature; (f) experimental G' and G'' data plotted against the single-mode Maxwell model for HEC90*5Np more closely describes these data, yet is still inadequate.

moduli works well within a narrow temperature window between $0 \leq T \leq 30^\circ\text{C}$ (see **Figure 2** and **Figure 3**), while failing slightly at low frequencies and higher temperatures ($T > 30^\circ\text{C}$). This behaviour is expected as it is common to observe variation in activation energies for relaxation processes in physical networks on account of varied distribution of transient crosslinkers.³⁶

Viscoelastic behaviours of most supramolecular networks at various temperatures may be superimposed using a single horizontal shift factor.^{35,37–40} By contrast, the frequency-dependent viscoelastic moduli of complex materials can only be superimposed using two shift factors (**Figure S5**), describing the activation energy of the relaxation process and change in the density of the polymer network with temperature.^{40,41} The vertical shifts are required for the construction of G' and G'' master curves because the network density changes with temperature, as reported previously in polymer networks assembled from adamantyl and β -cyclodextrin host-guest interactions⁴² and hydrogen bonded poly(*n*-butyl) acrylate chains functionalised with triurea moieties.²⁴ Deviation of the vertical shifts observed at higher temperatures is most likely attributed to rapid association-dissociation kinetics of CB[8] host-guest complexes at higher temperatures, thereby weakening the interchain crosslinking in the networks. Nevertheless, CB[8] inclusion complexes are known to possess high thermodynamic stability despite the fast associative and dissociative processes.⁸ Hence, nearly 90%

CB[8]-based ternary complexes remain in closed state at 50°C , maintaining a high degree of chain connectivity throughout the polymer networks (**Figures 3e**).

In physically-crosslinked networks, the crossover angular frequency (ω_c), where $G' = G''$, can be taken as a characteristic relaxation time of the network (τ_c).^{11,43} Thus, at $\omega > 1/\tau_c$, a material behaves more elastic-like, storing more energy than it dissipates, while at $\omega < 1/\tau_c$ the material exhibits liquid-like behaviour, dissipating more energy than it can store. The relaxation time of the reversible network is dependent implicitly on the open-state of a crosslink, and not dictated explicitly by the lifetime of the crosslink.¹³ At 0.5 wt.% HEC-Np loading, HEC1300*5Np and HEC250*5Np formed viscoelastic hydrogels, with the storage modulus (G') greater than the loss modulus (G'') over a broad range of frequencies. Indeed, these materials became increasingly more elastic with increasing polymer molecular weight, as evidenced by the shift of the ω_c towards lower frequencies for the HEC250*5Np and HEC1300*5Np networks (**Figures 2a, 2b**), which corroborated macroscopic observations using inverted vial tests (**Figure S1**). These supramolecular polymer networks also displayed thermoresponsiveness, exhibiting hydrogel-like behaviour at room temperature, yet behaving fluid-like at elevated temperatures (**Figure S6**). In contrast, the network prepared from HEC90*5Np polymer was observed to behave like a viscoelastic fluid even at room temperature, only turn-

ing weakly elastic at $\omega_c > 10 \text{ rad s}^{-1}$ (Figure 2c).

Previously, viscoelasticity of CB[8] physical networks built from low molecular weight polymeric precursors ($M_n < 20 \text{ kDa}$) was assumed to obey a single-mode Maxwell model (typically applied to describe viscoelastic materials with a single characteristic relaxation time) driven primarily by the supramolecular crosslinking.²⁹ The relaxation behaviour of our current system, though, was designed to be more complicated, representing a combination of two timescales: (i) the fast-mode associated to the guest exchange in CB[8]-based crosslinks and (ii) the slow-mode which is a cumulative effect of the network relaxation.⁴⁴ For this reason, we exploited an approach used previously in the characterisation of complex relaxation behaviour of polymeric systems,^{11,45} whereby an infinite spectrum of relaxation times, denoted as $H(\tau)$, is derived from experimental G' and G'' values (Figures 2d - 2f). In Figures 2a - 2c, the fitted relaxation spectra from Figures 2d - 2f, correlate well with the experimental viscoelastic moduli of each network.

Interestingly, the HEC90*5Np-based materials exhibited a single relaxation mode at $1/\tau = 10^2 \text{ rad s}^{-1}$, corresponding to the relaxation of polymer chain by breaking few transient CB[8] crosslinks at a time⁴⁶ (Figure 2f). This corroborates previous observations with CB[8]-based systems using low molecular weight polymer precursors.²⁹ In contrast, more complex relaxation behaviour was detected in the HEC1300*5Np and HEC250*5Np ensembles (Figures 2d, 2e). Deconvolution of their relaxation spectra identified two mechanically distinct relaxation modes, including a fast dissipative mode occurring at $1/\tau = 10^2 \text{ rad s}^{-1}$ which overlays with the single peak in the HEC90*5Np system (Figures 2c - 2d, Figure 5b). A second relaxation mode observed at timescales of $1/\tau = 10^{-2} - 10^2 \text{ rad s}^{-1}$ shifted towards lower $1/\tau$ as a function of polymer molecular weight (Figure 5a). The higher crosslink content on the high molecular weight HEC*5Np alter the static elasticity of the networks at frequencies below ω_c , primarily reflecting the polydispersity effect of chain length in hindering the network relaxation.³² In the long timescale, the anisotropy of the chain conformation decays under the applied strain through the Rouse-like chain motion⁴⁷ triggered by the partial-sequential decomplexation of the crosslinkers on the chain of the gel network, as suggested by Olsen and Tang.⁴³

By determining $H(\tau)$ for a series of polymer networks with identical crosslinking dynamics and concentration of functional crosslinks, we can identify the slower and broader dissipation mode as the polymer-driven stress relaxation mode, while the fast dissipation mode corresponds to the dynamic CB[8] host-guest inclusion complexes, as seen in overlays of the two relaxation modes (Figure 5a - 5b). Interestingly, the timescale and magnitude of the CB[8]·MV·Np-associated relaxation mode can be estimated from Figure 5b, where the lifetime of the relaxation mode corresponds to the lifetime of the supramolecular complex⁸ and the area under the peak is proportional to the relaxation time of the corresponding HEC-Np polymer (Figure 5a, inset). Moreover, these observations corroborate the molecular weight dependence of τ_c described above (Figure 3d). When fitting a power law to the upper two out of three data, a scaling exponent of 2 is obtained, which is in qualitative agreement with

Rouse scaling for the higher molecular weight HEC*5Np polymers. It is only when a molecular-weight dependent relaxation mode is observed that Rouse-like scaling behaviour holds, as a large deviation from this behaviour is observed in the case of HEC90*5Np, which does not display a molecular-weight dependent relaxation mode. Comparing the experimental rheological data with the “sticky Rouse” model³⁵ demonstrates dramatic inconsistency (Figure 3a - 3c), indicating that these systems are not adequately described by this model. Additionally, the comparison of a single-mode Maxwell model to the HEC90*5Np system insufficiently describes the experimental data (Figure 3f). Even though a single relaxation mode is observed in this system that is specifically correlated with the dissociation of the host-guest complex, this observation demonstrates that this relaxation mode must exhibit some dispersity in its characteristic timescale. Furthermore, the global Arrhenius activation energies (E_a) for network relaxation calculated from the temperature dependence of a_T from TTS demonstrates molecular weight dependence (Figure 5c). The activation energies vary slightly with τ_c , indicating that the E_a for network relaxation is primarily dictated by the structural hierarchy coupled with temporal kinetics.

2.2 Determination of the contribution of supramolecular dynamics to mechanical performance

The strength of dynamically crosslinked polymeric systems has been tied to the lifetime of the supramolecular interactions, and thus ultimately to the dissociation and guest exchange of the supramolecular crosslink.^{8,20} Dissociation constants for CB[8]-based ternary complexes vary significantly according to structure and electronic properties of the second guest (G2),^{8,48} although the overall equilibrium binding constants (K_{eq}) can often be similar for certain sets of second guest moieties. Our group previously sought to isolate the effects of supramolecular crosslinking on the bulk macroscopic properties of CB[8]-based materials by developing a system of hydrogels identical in every way, except the molecular structure of the second guest appended to the polymer chains.⁸ The guests used include pyrenyl (Pyr), dibenzofuranyl (Dbf), and naphthyl (Np) moieties and display a range of exchange dynamics, characterised by the dissociation rate constant (k_d : Pyr < Dbf < Np) and the energetic barrier to dissociation (E_{ad} : Pyr > Dbf > Np). We observed that the elasticity of the materials prepared with each moiety was directly impacted by the supramolecular dynamics, whereby Pyr gave the most elastic materials, followed by Dbf, and finally Np.⁸ To better understand the stress dissipative modes in supramolecular polymer networks, we employed three different crosslinking systems within the HEC1300-based polymer networks. Utilising protocols adapted from literature,⁸ we modified HEC1300 with two other second guests, Dbf and Pyr, at the same molar loading as our HEC-Np polymers (5 mol%), yielding HEC1300*5Dbf and HEC1300*5Pyr. Again, frequency-dependent master curves were prepared with TTS for comparison with the HEC1300*5Np materials demonstrated above.

On account of slower dissociation of Dbf and Pyr-based ternary complexes, τ_c was not observed for either system across the

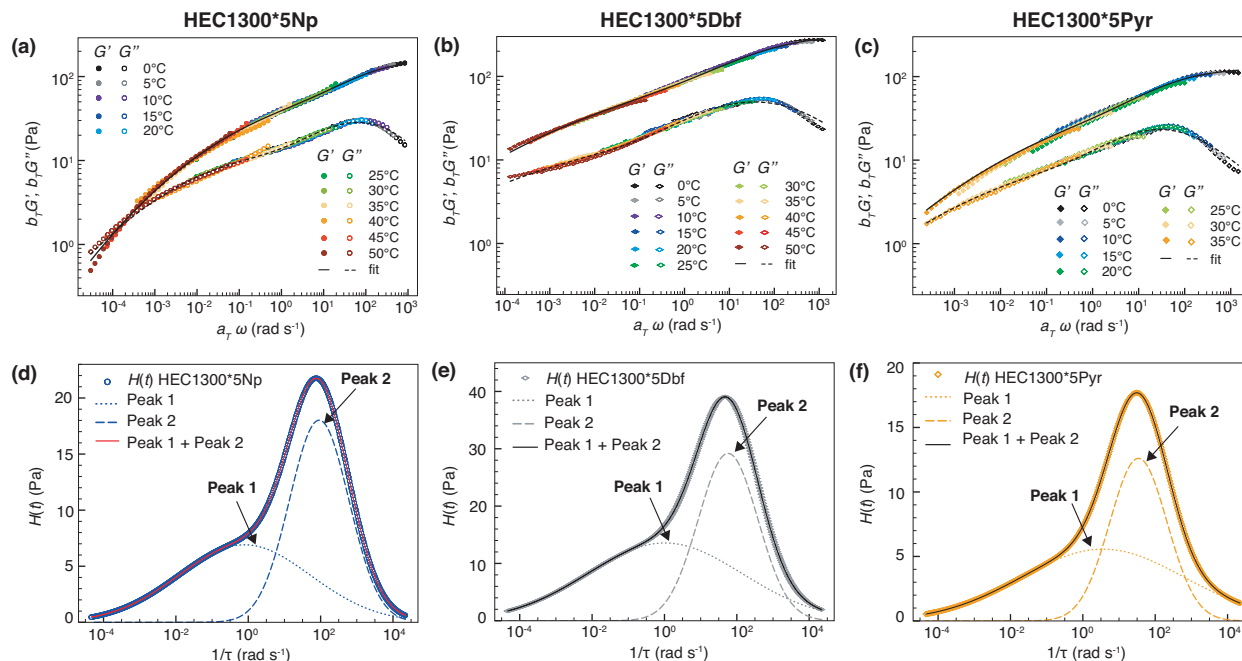


Fig. 4 Master curves of the viscoelastic moduli for (a) HEC1300*5Np, (b) HEC1300*5Dbf, and (c) HEC1300*5Pyr networks referenced to 20 °C. (d - f) Relaxation spectra of CB[8]-assisted supramolecular polymer networks consisting of different second guests, showing double peaks in G'' as seen in **Figure 2d**. The two local maxima in G'' in each HEC1300 network are indicative of two distinct relaxation mode distributions, which can fit to the relaxation spectra $H(\tau)$. The master curve and relaxation spectrum of the HEC1300*5Np network are included for comparison purposes.

experimental timescales (**Figures 4b - 4c**). The substantial downshift of τ_c , followed by the proportional increase in storage moduli in these networks with strong crosslinkers (Dbf and Pyr moieties) are in good agreement with previous reports.^{32,49,50} From their relaxation spectra, all three materials clearly exhibited two distinct relaxation modes (**Figures 4e - 4f**). As all three materials were prepared with HEC1300 polymers, they exhibit a similar slow molecular weight dependent relaxation mode (**Figure 5d**), regardless of the presence of kinetically-distinct dynamic crosslinking between polymer chains. In contrast, the fast relaxation mode exhibits a guest-dependent shift in the peak relaxation lifetime (**Figure 5e**) commensurate with the binding dynamics of the various second guests, whereby, for example, the HEC1300*5Pyr network demonstrates the slowest relaxation lifetime of the set as the dissociation kinetics of the Pyr-based ternary complexes is the slowest among the second guests employed. Indeed, a plot of the peak relaxation lifetime from **Figure 5e** against the reported k_d for these guests⁸ gives a linear relationship with an R^2 value of 0.9999. Moreover, the E_a for network relaxation exhibits no significant dependence on the different supramolecular crosslinking dynamics (**Figure 5f**), supporting our previous observations that this global E_a value is primarily dictated by the slower, molecular weight dependent relaxation mode. This further proves that the TTS principle is valid for our transient systems exhibiting a dominant relaxation mechanism, where a single E_a clearly tracks with the molecular weight of the polymers. The present experiments not only complement our previous study⁸ but also recent systematic studies by Alvarez *et al.*,⁴⁹ Holten-Andersen *et al.*⁵¹

and Seiffert³² for various supramolecular systems.

3 Conclusion

In summary, we have demonstrated a simple approach to distinguish the relaxation dynamics of complex physically crosslinked materials. Decoupling the impact of the supramolecular crosslinking motifs from the polymer structure and vice versa allows for remarkable control of each hierarchy to orthogonally modulate the bulk mechanical properties and relaxation behaviour of these dynamic materials. Below the entanglement molecular weight, the macroscopic mechanical properties of these materials are predominantly controlled by the exchange kinetics of the supramolecular crosslinkers, yielding a single fast relaxation mode with a lifetime commensurate with the crosslinking exchange kinetics. Yet, increasing polymer molecular weight, and thus the number of crosslinks per chain, while keeping the crosslink density constant yields a second, mechanically distinct, and molecular weight dependent slow relaxation mode. Moreover, by employing a set of kinetically distinct supramolecular moieties, it is possible to clearly identify the fast relaxation mode as being determined by the supramolecular dynamics, as this mode shifts to longer timeframes for crosslinking motifs exhibiting slower binding kinetics. We envisage the results presented here can inform a general strategy to engineer novel supramolecular materials through the manipulation of both the temporal and structural hierarchy of these highly functional soft materials.

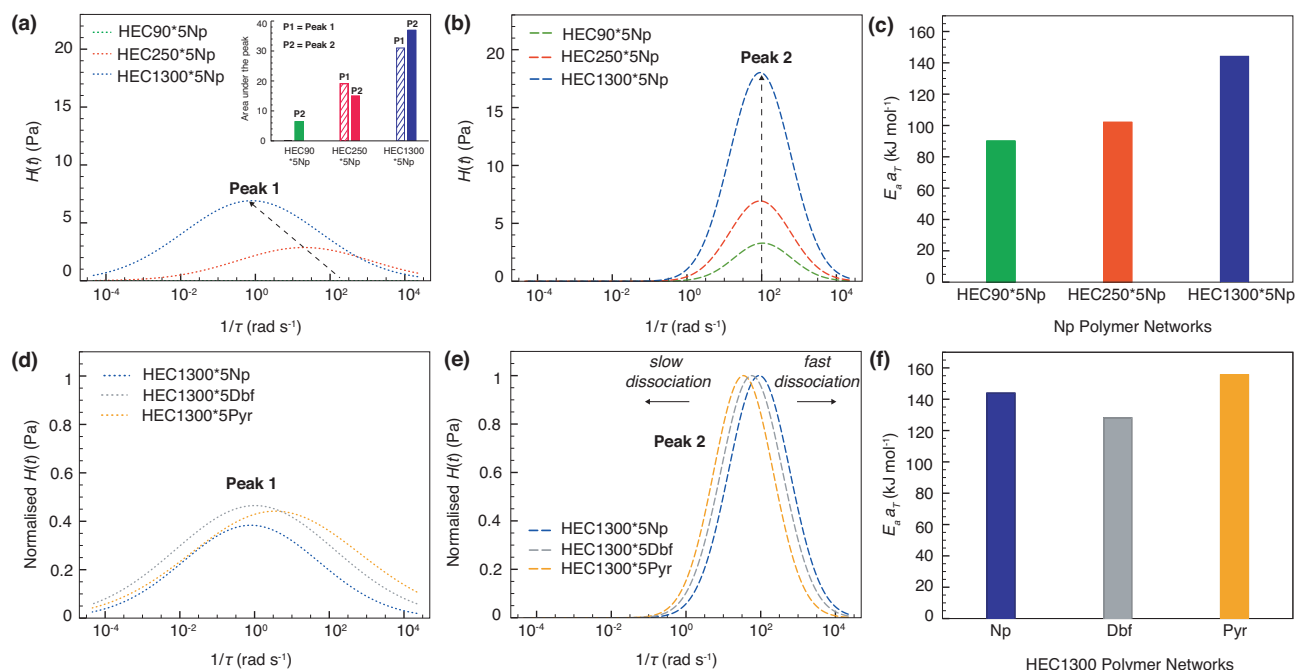


Fig. 5 Deconvoluted peaks from the infinite relaxation spectra $H(\tau)$ formed by CB[8]·MV·G2 heteroternary complexation demonstrating the relative contributions of (a/b) polymer molecular weight and (d/e) guest dynamics to the overall relaxation behaviour. (a) The polymer-associated peak from CB[8]·MV·Np networks shifts towards lower ω with increasing polymer molecular weight, while (b) the supramolecular crosslinking-associated peak appears aligned and the magnitude of energy dissipation (area under the peak) increases as a function of molecular weight (see inset in (a)). These data highlight that the relative magnitudes of the energy dissipation modes can be controlled simply by changing the polymer molecular weight. (c) Arrhenius activation energies (E_a) for the network relaxation calculated from the temperature dependence of a_T for HEC-Np based networks of different polymer molecular weights. (d) The slow mode peaks from CB[8]·MV·G2 networks are similar for all systems as they are all prepared from HEC1300 polymers, while (e) the fast-mode peaks shift towards lower ω in accordance with the dissociation dynamics of second guest from the CB[8]·MV binary complex. (f) Arrhenius activation energies (E_a) for the network relaxation for HEC1300-based polymer networks with various second guests.

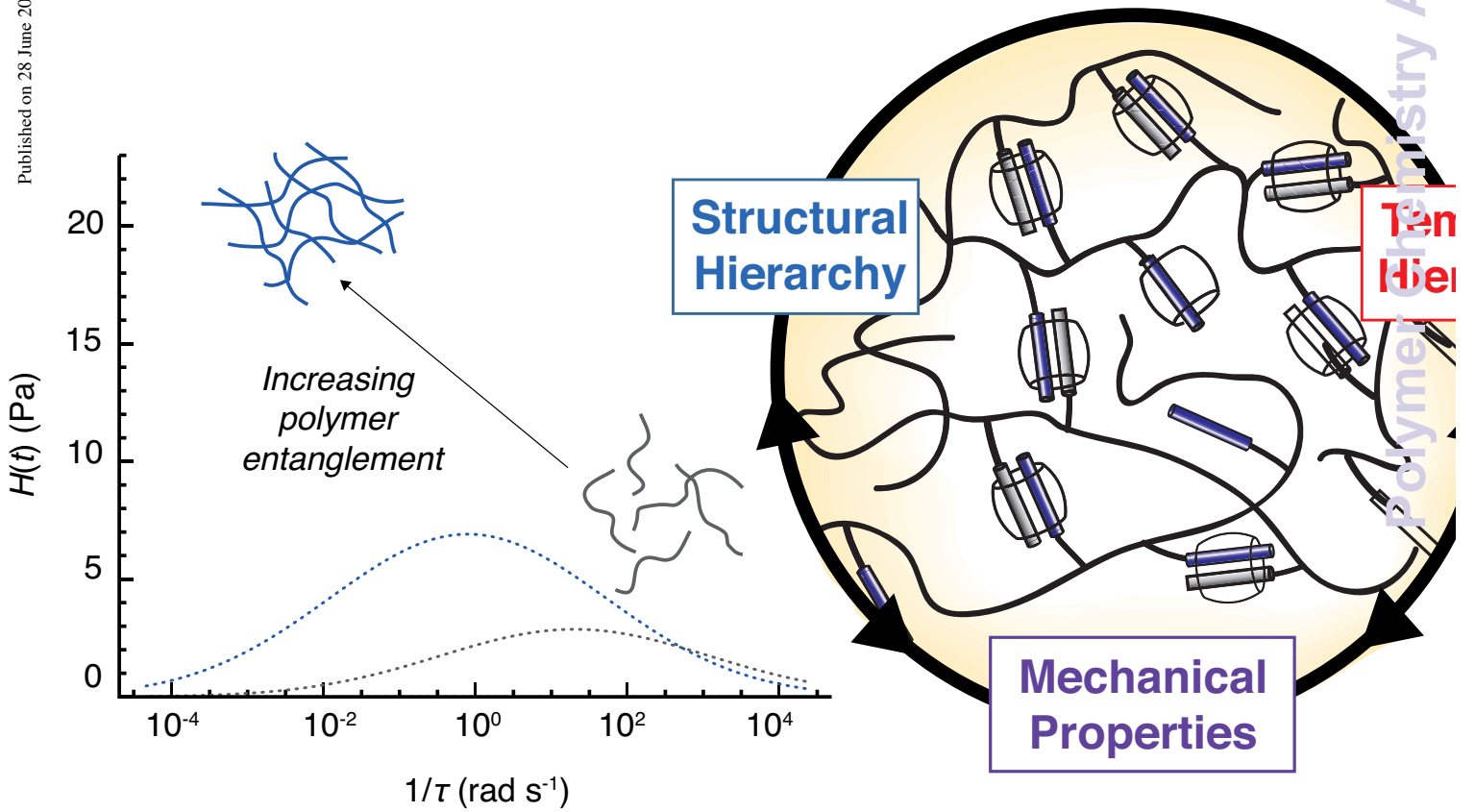
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References

- J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv. Mater.*, 2003, **15**, 1155–1158.
- J.-Y. Sun, X. Zhao, W. R. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. Suo, *Nature*, 2012, **489**, 133–136.
- J. Liu, C. S. Y. Tan, Z. Yu, Y. Lan, C. Abell and O. A. Scherman, *Adv. Mater.*, 2017, **29**, 1604951.
- J. Liu, C. S. Y. Tan, Z. Y. Yu, N. Li, C. Abell and O. A. Scherman, *Adv. Mater.*, 2017, **29**, 1605325.
- J. Liu, C. S. Y. Tan, Y. Lan and O. A. Scherman, *J. Polym. Sci. A Polym. Chem.*, 2017, **In Press**, DOI:10.1002/pola.20170260.
- E.-R. Janeček, J. R. McKee, C. S. Y. Tan, A. Nykänen, M. Ketunen, J. Laine, O. Ikkala and O. A. Scherman, *Angew. Chem. Int. Ed.*, 2015, **54**, 5383–5388.
- C. B. Rodell, N. N. Dusaj, C. B. Highley and J. A. Burdick, *Adv. Mater.*, 2016, **28**, 8419–8424.
- E. A. Appel, R. A. Forster, A. Koutsioubas, C. Toprakcioglu and O. A. Scherman, *Angew. Chem. Int. Ed.*, 2014, **53**, 10038–10043.
- P. H. Kouwer, M. Koepf, V. A. Le Sage, M. Jaspers, A. M. van Buul, Z. H. Eksteen-Akeroyd, T. Woltinge, E. Schwartz, H. J. Kitto, R. Hoogenboom *et al.*, *Nature*, 2013, **493**, 651–655.
- R. Wang, M. K. Sing, R. K. Avery, B. S. Souza, M. Kim and B. D. Olsen, *Acc. Chem. Res.*, 2016, **49**, 2786–2795.
- S. C. Grindy, R. Learsch, D. Mozhdehi, J. Cheng, D. G. Barrett, Z. Guan, P. B. Messersmith and N. Holten-Andersen, *Nat. Mater.*, 2015, **14**, 1210–1216.
- M. Guo, L. M. Pitet, H. M. Wyss, M. Vos, P. Y. Dankers and E. Meijer, *J. Am. Chem. Soc.*, 2014, **136**, 6969–6977.
- L. Leibler, M. Rubinstein and R. H. Colby, *Macromolecules*,

- 1991, **24**, 4701–4707.
- 14 M. Rubinstein and A. N. Semenov, *Macromolecules*, 1998, **31**, 1386–1397.
- 15 A. N. Semenov and M. Rubinstein, *Macromolecules*, 1998, **31**, 1373–1385.
- 16 M. Green and A. Tobolsky, *J. Chem. Phys.*, 1946, **14**, 80–92.
- 17 A. Lodge, *Trans. Faraday Soc.*, 1956, **52**, 120–130.
- 18 F. Tanaka and S. Edwards, *Macromolecules*, 1992, **25**, 1516–1523.
- 19 D. Mozhdehi, J. A. Neal, S. C. Grindy, Y. Cordeau, S. Ayala, N. Holten-Andersen and Z. Guan, *Macromolecules*, 2016, **49**, 6310–6321.
- 20 W. C. Yount, D. M. Loveless and S. L. Craig, *Angew. Chem.*, 2005, **117**, 2806–2808.
- 21 Q. Li, D. G. Barrett, P. B. Messersmith and N. Holten-Andersen, *ACS Nano*, 2016, **10**, 1317–1324.
- 22 S. Tang, A. Habicht, S. Li, S. Seiffert and B. D. Olsen, *Macromolecules*, 2016, **49**, 5599–5608.
- 23 S. Hackelbusch, T. Rossow, P. van Assenbergh and S. Seiffert, *Macromolecules*, 2013, **46**, 6273–6286.
- 24 X. Callies, C. Véchambre, C. Fonteneau, S. Pensec, J.-M. Chenal, L. Chazeau, L. Bouteiller, G. Ducouret and C. Creton, *Macromolecules*, 2015, **48**, 7320–7326.
- 25 M. Ahmadi, L. G. D. Hawke, H. Goldansaz and E. van Ruymbeke, *Macromolecules*, 2015, **48**, 7300–7310.
- 26 J. Liu, C. S. Y. Tan, Y. Lan and O. A. Scherman, *Macromol. Chem. Phys.*, 2016, **217**, 319–332.
- 27 J. Liu, Y. Lan, Z. Y. Yu, C. S. Y. Tan, R. M. Parker, C. Abell and O. A. Scherman, *Acc. Chem. Res.*, 2017, **50**, 208–217.
- 28 C. S. Y. Tan, J. del Barrio, J. Liu and O. A. Scherman, *Polym. Chem.*, 2015, **6**, 7652–7657.
- 29 E. A. Appel, F. Biedermann, U. Rauwald, S. T. Jones, J. M. Zayed and O. A. Scherman, *J. Am. Chem. Soc.*, 2010, **132**, 14251–14260.
- 30 J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540–541.
- 31 U. Rauwald, F. Biedermann, S. Deroo, C. V. Robinson and O. A. Scherman, *J. Phys. Chem. B*, 2010, **114**, 8606–8615.
- 32 S. Seiffert, *Macromol. Rapid Commun.*, 2016, **37**, 257–264.
- 33 F. Biedermann, E. A. Appel, J. Del Barrio, T. Gruending, C. Barner-Kowollik and O. A. Scherman, *Macromolecules*, 2011, **44**, 4828–4835.
- 34 M. Rubinstein and A. N. Semenov, *Macromolecules*, 2001, **34**, 1058–1068.
- 35 K. E. Feldman, M. J. Kade, E. W. Meijer, C. J. Hawker and E. J. Kramer, *Macromolecules*, 2009, **42**, 9072–9081.
- 36 T. L. Sun, T. Kurokawa, S. Kuroda, A. B. Ihsan, T. Akasaki, K. Sato, M. A. Haque, T. Nakajima and J. P. Gong, *Nat. Mater.*, 2013, **12**, 932–937.
- 37 Y. Lei and T. P. Lodge, *Soft Matter*, 2012, **8**, 2110–2120.
- 38 A. Noro, Y. Matsushita and T. P. Lodge, *Macromolecules*, 2008, **41**, 5839–5844.
- 39 A. Noro, Y. Matsushita and T. P. Lodge, *Macromolecules*, 2009, **42**, 5802–5810.
- 40 S. Seiffert and J. Sprakel, *Chem. Soc. Rev.*, 2012, **41**, 909–930.
- 41 R. K. Castellano, R. Clark, S. L. Craig, C. Nuckolls and J. Rebek, *Proc. Natl. Acad. Sci. U.S.A.*, 2000, **97**, 12418–12421.
- 42 L. Li, X. Guo, J. Wang, P. Liu, R. K. Prud'homme, B. L. May and S. F. Lincoln, *Macromolecules*, 2008, **41**, 8677–8681.
- 43 S. Tang and B. D. Olsen, *Macromolecules*, 2016, **49**, 9163–9175.
- 44 P. Wood-Adams and S. Costeux, *Macromolecules*, 2001, **34**, 6281–6290.
- 45 T. Annable, R. Buscall, R. Ettelaie and D. Whittlestone, *J. Rheol (1978-present)*, 1993, **37**, 695–726.
- 46 M. Rubinstein and A. N. Semenov, *Macromolecules*, 2001, **34**, 1058–1068.
- 47 H. Watanabe, *Prog. Polym. Sci.*, 1999, **24**, 1253–1403.
- 48 U. Rauwald, F. Biedermann, S. Deroo, C. V. Robinson and O. A. Scherman, *J. Phys. Chem. B*, 2010, **114**, 8606–8615.
- 49 A. Shabbir, H. Goldansaz, O. Hassager, E. van Ruymbeke and N. J. Alvarez, *Macromolecules*, 2015, **48**, 5988–5996.
- 50 C. L. Lewis, K. Stewart and M. Anthamatten, *Macromolecules*, 2014, **47**, 729–740.
- 51 S. C. Grindy, M. Lenz and N. Holten-Andersen, *Macromolecules*, 2016, **49**, 8306–8312.



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