

Supramolecular Cross-Linked Networks *via* Host–Guest Complexation with Cucurbit[8]uril

Eric A. Appel, Frank Biedermann, Urs Rauwald, Samuel T. Jones, Jameel M. Zayed, and Oren A. Scherman*

Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

Received July 18, 2010; E-mail: oas23@cam.ac.uk

Abstract: The ability to finely tune the solution viscosity of an aqueous system is critical in many applications ranging from large-scale fluid-based industrial processes to free-standing hydrogels important in regenerative medicine, controlled drug delivery, and ‘green’ self-healing materials. Herein we demonstrate the use of the macrocyclic host molecule cucurbit[8]uril (CB[8]) to facilitate reversible cross-linking of multivalent copolymers with high binding constants ($K_a > 10^{11}–10^{12} \text{ M}^{-2}$) leading to a supramolecular hydrogel. Multivalent copolymers were prepared by free radical polymerization techniques and contained either pendant methyl viologen (a good first guest for CB[8]) or naphthoxy derivatives (good second guests for CB[8]). A colorless solution of the two multivalent copolymers bearing first and second guests, respectively, can be transformed into a highly viscous, colored supramolecular hydrogel with the cross-link density being easily controlled through CB[8] addition. Moreover, the cross-links (1:1:1 supramolecular ternary complexes of CB[8]/viologen/naphthoxy) are dynamic and stimuli-responsive, and the material properties can be modulated by temperature or other external stimuli. Rheological characterization of the bulk material properties of these dynamically cross-linked networks provided insight into the kinetics of CB[8] ternary complexation responsible for elastically active cross-linking with a second guest dissociation rate constant (k_d) of 1200 s^{-1} for the ternary complex. These materials exhibited intermediate mechanical properties at 5 wt % in water (plateau modulus = 350–600 Pa and zero-shear viscosity = 5–55 Pa·s), which is complementary to existing supramolecular hydrogels. Additionally, these supramolecular hydrogels exhibited thermal reversibility and subsequent facile modulation of microstructure upon further addition of CB[8] and thermal treatment. The fundamental knowledge gained from the study of these dynamic materials will facilitate progress in the field of smart, self-healing materials, self-assembled hydrogels, and controlled solution viscosity.

Introduction

Supramolecular assembly encompasses the formation of structurally well-defined aggregates associated noncovalently with reversible interactions tunable by external stimuli.¹ The desire to dictate and control the macroscopic properties of polymeric materials has, in part, grown from the success of the rational design of well-defined supramolecular interactions through small-molecule synthesis.^{2–5} Self-assembled polymeric materials have proven to act as ‘smart’ matter with specific stimuli-responsive material properties on the macroscopic level.^{6–10} These materials take advantage of specific, directional noncovalent interactions that are

tunably responsive to various external stimuli including solvent composition, pH, temperature, salt concentration, electric potential, and light. Self-assembled materials have led to the preparation of supramolecular polymers,^{11–13} cross-linked gel materials,^{14–16} hierarchical assemblies,^{17,18} metal-nanoparticle assemblies,^{19,21} and metastable polymeric nanoparticles.^{22,23}

Supramolecular polymeric hydro- and organogels have received much focus recently on account of the mechanical properties gained from use of polymeric building blocks and also the stimuli responsivity and processability inherent to the supramolecular units used in cross-linking. Previously, organic

- (1) Whitesides, G.; Mathias, J.; Seta, C. *Science* **1991**, *254*, 1312–1319.
- (2) Steed, J.; Atwood, J. *Supramolecular chemistry*; Wiley: New York: 2000.
- (3) Lehn, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304–1319.
- (4) Reinhoudt, D.; Atwood, J.; Lehn, J. *Comprehensive Supramolecular Chemistry*; Pergamon Press: 1996.
- (5) Lehn, J. M. *Supramolecular chemistry: concepts and perspectives*; Wiley VCH: 1995.
- (6) Peng, F.; Li, G.; Liu, X.; Wu, S.; Tong, Z. *J. Am. Chem. Soc.* **2008**, *130*, 16166–16167.
- (7) Zhang, Y.; Yang, Z.; Yuan, F.; Gu, H.; Gao, P.; Xu, B. *J. Am. Chem. Soc.* **2004**, *126*, 15028–15029.
- (8) Ma, M.; Kuang, Y.; Gao, Y.; Zhang, Y.; Gao, P.; Xu, B. *J. Am. Chem. Soc.* **2010**, *132*, 2719–2728.
- (9) Patra, T.; Pal, A.; Dey, J. *Langmuir* **2010**, *26*, 7761–7767.

- (10) Zhao, Y.-L.; Stoddart, J. F. *Langmuir* **2009**, *25*, 8442–8446.
- (11) Greef, T. F. A. D.; Smulders, M. M. J.; Wolfs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687–5754.
- (12) Brunsveld, L.; Folmer, B.; Meijer, E.; Sijbesma, R. *Chem. Rev.* **2001**, *101*, 4071–4097.
- (13) Dankers, P.; Meijer, E. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2047–2073.
- (14) Lange, R.; Gulp, M. V.; Meijer, E. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657–3670.
- (15) Feldman, K.; Kade, M.; Meijer, E.; Hawker, C.; Kramer, E. *Macromolecules* **2009**, *42*, 9072–9081.
- (16) Wang, Q.; Mynar, J. L.; Yoshida, M.; Lee, E.; Lee, M.; Okuro, K.; Kinbara, K.; Aida, T. *Nature* **2010**, *463*, 339–343.
- (17) Rauwald, U.; Scherman, O. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3950–3953.

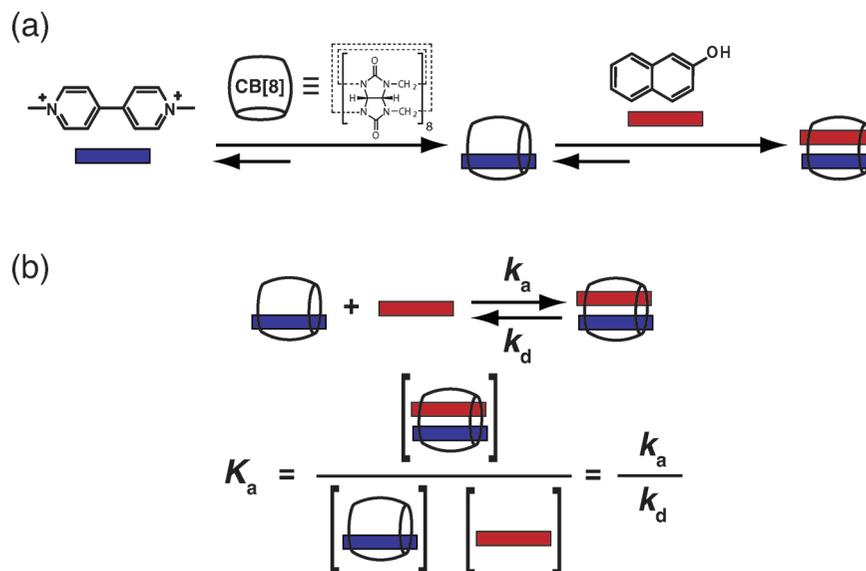


Figure 1. (a) Schematic of the two-step, three-component binding of cucurbit[8]uril in water. (b) Thermodynamic and kinetic parameters of second-guest binding.

polymer hydrogels have been demonstrated utilizing the well-known cyclodextrin (CD)/adamantane (Ad) two-component complementary binding motif.^{24,25} Ritter and co-workers demonstrated the preparation of a random copolymer consisting of *N*-isopropylacrylamide (NIPAM) and Ad-functional acrylamide monomeric units ($M_n \approx 50$ –75 kDa). Hydrogels formed from the mixture of this copolymer and a discrete CD-dimer had modest properties ($\eta_o = 1$ –10 Pa·s @ 7.5 wt %) that could be altered as a function of the lower critical solution temperature (LCST) of the NIPAM-containing copolymer.²⁵ The authors subsequently demonstrated a system with greatly increased mechanical properties ($\eta_o = 100$ –1000 Pa·s @ 10 wt %) from a similar copolymer of the Ad-functional monomer copolymerized with a negatively charged monomer ($M_n \approx 125$ kDa) and a globular CD polymer ($M_n \approx 90$ kDa).²⁴ Recently, supramolecular polymer–clay hybrid hydrogels have been reported that use multivalent ionic interactions from telechelic poly(ethylene glycol)s bearing guanidinium-functional dendritic end groups with clay nanosheets that are surface-coated with poly(sodium acrylate).¹⁶ These hydrogels exhibit very high mechanical strength (10^4 – 10^6 Pa), rapid self-healing ability, and stimuli responsiveness and can be formed into shape-persistent, free-standing macroscopic objects.

Another family of macrocyclic host molecules is cucurbit[*n*]uril (CB[*n*]), which are cyclic, methylene-linked oligomers of glycoluril that have a symmetric ‘barrel’ shape with two identical portal regions laced by ureido-carbonyl oxygens. The number

of glycoluril units determines the size of the cucurbituril cavity without affecting the height of the molecular container (approximately 0.9 nm), similar to the case for the CD family. While CB[5], CB[6], and CB[7] are all capable of binding single guests (typically cationic amines, metal or imidazolium ions),^{26–29} CB[8] has a larger cavity volume of 479 Å³ and can simultaneously accommodate two guests (Figure 1a).^{30,31} An electron-deficient first guest such as viologen (MV) and an electron-rich second guest such as 2-naphthol form a stable 1:1:1 ternary complex with CB[8] through multiple noncovalent interactions acting synergistically, including electrostatic and hydrophobic effects. This ternary complex is accompanied by the quantitative formation of a new visible absorbance on account of formation of a charge-transfer complex between the MV and naphthol groups. The utility of CB[8] as a dynamic interlink between MV and a variety of electron-rich aromatic guests has been demonstrated, exhibiting reversible redox-responsive behavior.^{32–35} The formation of ternary complexes with CB[8] occurs in a stepwise binding process whereby the electron-poor guest enters first (K_{a1}) followed by the electron-rich guest (K_{a2}). While there are two K_a values associated with this binding scheme (resulting in the overall K reported in M⁻²), focus may be placed on the dynamic equilibrium and kinetics of the second guest binding (Figure 1b)

- (18) ten Brinke, G.; Ruokolainen, J.; Ikkala, O. *Adv. Polym. Sci.* **2007**, *207*, 113–177.
 (19) Celiz, A. D.; Lee, T.-C.; Scherman, O. A. *Adv. Mater.* **2009**, *21*, 3937–3940.
 (20) Boal, A.; Ilhan, F.; DeRouchey, J.; Thurn-Albrecht, T.; Russell, T.; Rotello, V. *Nature* **2000**, *404*, 746–748.
 (21) Liu, J.; Mendoza, S.; Roman, E.; Lynn, M.; Xu, R.; Kaifer, A. *J. Am. Chem. Soc.* **1999**, *121*, 4304–4305.
 (22) Foster, E.; Berda, E.; Meijer, E. *J. Am. Chem. Soc.* **2009**, *131*, 6964–6966.
 (23) Seo, M.; Beck, B. J.; Paulusse, J. M. J.; Hawker, C. J.; Kim, S. Y. *Macromolecules* **2008**, *41*, 6413–6418.
 (24) Koopmans, C.; Ritter, H. *Macromolecules* **2008**, *41*, 7418–7422.
 (25) Kretschmann, O.; Choi, S.; Miyauchi, M.; Tomatsu, I.; Harada, A.; Ritter, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 4361–4365.

- (26) Zhao, N.; Liu, L.; Biedermann, F.; Scherman, O. A. *Chem.—Asian J.* **2010**, *5*, 530–537.
 (27) Marquez, C.; Hudgins, R.; Nau, W. *J. Am. Chem. Soc.* **2004**, *126*, 5806–5816.
 (28) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870.
 (29) Liu, S.; Ruspic, C.; Mukhopadhyay, P.; Chakrabarti, S.; Zavalij, P.; Isaacs, L. *J. Am. Chem. Soc.* **2005**, *127*, 15959–15967.
 (30) Day, A.; Arnold, A.; Blanch, R.; Snushall, B. *J. Org. Chem.* **2001**, *66*, 8094–8100.
 (31) Kim, J.; Jung, I.; Kim, S.; Lee, E.; Kang, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *J. Am. Chem. Soc.* **2000**, *122*, 540–541.
 (32) Ko, Y.; Kim, K.; Kang, J.; Chun, H.; Lee, J.; Sakamoto, S.; Yamaguchi, K.; Fetters, J.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 1932–1933.
 (33) Lee, J.; Kim, K.; Choi, S.; Ko, Y.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Chem. Commun.* **2002**, 2692–2693.
 (34) Kim, K.; Kim, D.; Lee, J.; Ko, Y.; Kim, K. *Chem. Commun.* **2004**, 848–849.
 (35) Rauwald, U.; Biedermann, F.; Deroo, S.; Robinson, C. V.; Scherman, O. A. *J. Phys. Chem. B* **2010**, *114*, 8606–8615.

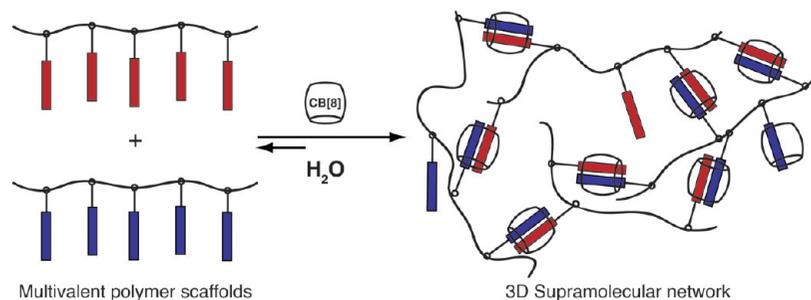


Figure 2. Supramolecular hydrogel preparation through addition of cucurbit[8]uril to a mixture of multivalent first and second guest functional polymers in water.

as this binding step is primarily responsible for the dissociation of the ternary complex.³⁵

The utility of CB[8] as a linking agent in polymeric and multivalent systems has been reported previously. Our group has recently demonstrated the CB[8]-mediated hierarchical self-assembly of amphiphilic diblock copolymers consisting of PEG_{5k} and polyisoprene_{10k} functionalized at their chain ends with MV and naphthoxy (Np) moieties, respectively.¹⁷ These polymers were found to subsequently form compartmentalized nanostructures upon complexation of their end groups inside CB[8]. This concept was extended further to the formation of ABA triblock copolymers using a small bifunctional unit coupling two end-functional PEG_{5k} polymers with CB[8].³⁶ Urbach and co-workers reported the self-assembly of multivalent receptors made from oligopeptides bearing either tryptophan residues or MV modified glutamine residues.³⁷

There have been a variety of reports concerning the formation of 3D polymeric networks and gels from noncovalent interactions in water; however, many of them are limited in use on account of (a) a lack of reversible stimuli responsivity, (b) toxic metal ions used for their formation, or (c) the use of a two-component binding motif providing little control over macroscopic material properties. In the present work, we strove to develop a system for the preparation of three-dimensional supramolecular cross-linked polymeric materials that utilizes the strong yet reversible CB[8]-based 1:1:1 ternary binding motif in water (Figure 2). Through the use of multivalent polymeric scaffolds of relatively low molecular weight ($M_n < 40$ kDa), bearing either MV or Np functionality pendant to the polymer backbone, we have developed a system for the preparation of supramolecular polymeric hydrogels. In the case of a typical two-component binding motif, mixing of the polymeric entities leads directly to gel formation. In contrast, the unique CB[8] three-component binding motif allows for greater control over bulk material properties through facile modulation of the cross-link density by inherently separating the two steps of polymeric solution preparation from cross-linking. Moreover, the well-known stimuli-responsive nature of the ternary complex and the ease of synthesis of the various components make this system well-suited for the preparation of supramolecular polymeric hydrogels.

Results and Discussion

Synthesis and Characterization of Functional Polymers. Free radical polymerization is arguably the most common polymer-

ization technique used for the production of commercially available polymers today. This is likely on account of several important features: (a) compatibility with a wide variety of monomers, including (meth)acrylates, (meth)acrylic acid, (meth)acrylamides, acrylonitrile, styrenics, dienes, vinyl acetate, and other vinyl monomers; (b) tolerance of unprotected functionalities in both monomer and solvent (e.g., $-\text{OH}$, $-\text{NR}_2$, $-\text{COOH}$, $-\text{CONR}_2$, and SO_3); (c) tolerance to aqueous or protic media; (d) compatibility with a variety of reaction conditions (e.g., bulk, solution, emulsion, and suspension); and (e) it is relatively inexpensive and easy, requiring simple starting materials without stringent or difficult practical implementation.^{38,39}

Herein we use radical polymerization in the preparation of two sets of multivalent side-chain functional polymers bearing either viologen (MV) **2a–c** (Scheme 1) or 2-naphthoxy (Np) **7a–c** (Scheme 2) derivatives. MV-functional copolymers **2a–c** were synthesized by traditional ‘uncontrolled’ free radical polymerization following a method substantially modified from one recently reported (Table 1).⁴⁰ A styrenic monomer bearing an MV moiety (STMV, **1**) was easily synthesized on a large scale from 4-vinylbenzylchloride and methyl bipyridinium iodide salt in high yields (>85%). Various comonomers with differing ionic nature (neutral, positive, or negative, see Scheme 1) were chosen in order to identify variations in the properties of the resulting supramolecular hydrogels arising from the structure of the parent polymers. *N*-Hydroxyethylacrylamide was a neutral, nonresponsive, water-soluble comonomer used to prepare copolymer **2a** which contained approximately 10 mol % loading of **1**. The copolymerization between various acrylamide monomers (including *N*-functional acrylamides) and styrenics has been investigated previously and demonstrated that copolymers were not completely random but formed gradient copolymers.^{41–43} Despite these observations however, the initial monomer concentration was retained in the isolated polymer (Table 1). (Vinylbenzyl)trimethylammonium chloride (SAM) and styrene sulfonate (SS) were chosen as positively and negatively charged styrenic comonomers for the synthesis of **2b** and **2c**, respectively. These polymers were prepared in the same manner as that for **2a** with a 10% loading of functional styrenic **1**. As the majority of the polymer weight, the ionic

- (36) (a) Deroo, S.; Rauwald, U.; Robinson, C. V.; Scherman, O. A. *Chem. Commun.* **2009**, 644–646. (b) Zayed, J. M.; Biedermann, F.; Rauwald, U.; Scherman, O. A. *Polym. Chem.* [Online early access]. DOI: 10.1039/C0PY00197J. Published Online: Sept 7, 2010.
 (37) Reczek, J. J.; Kennedy, A. A.; Halbert, B. T.; Urbach, A. R. *J. Am. Chem. Soc.* **2009**, *131*, 2408–2415.

(38) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669–692.

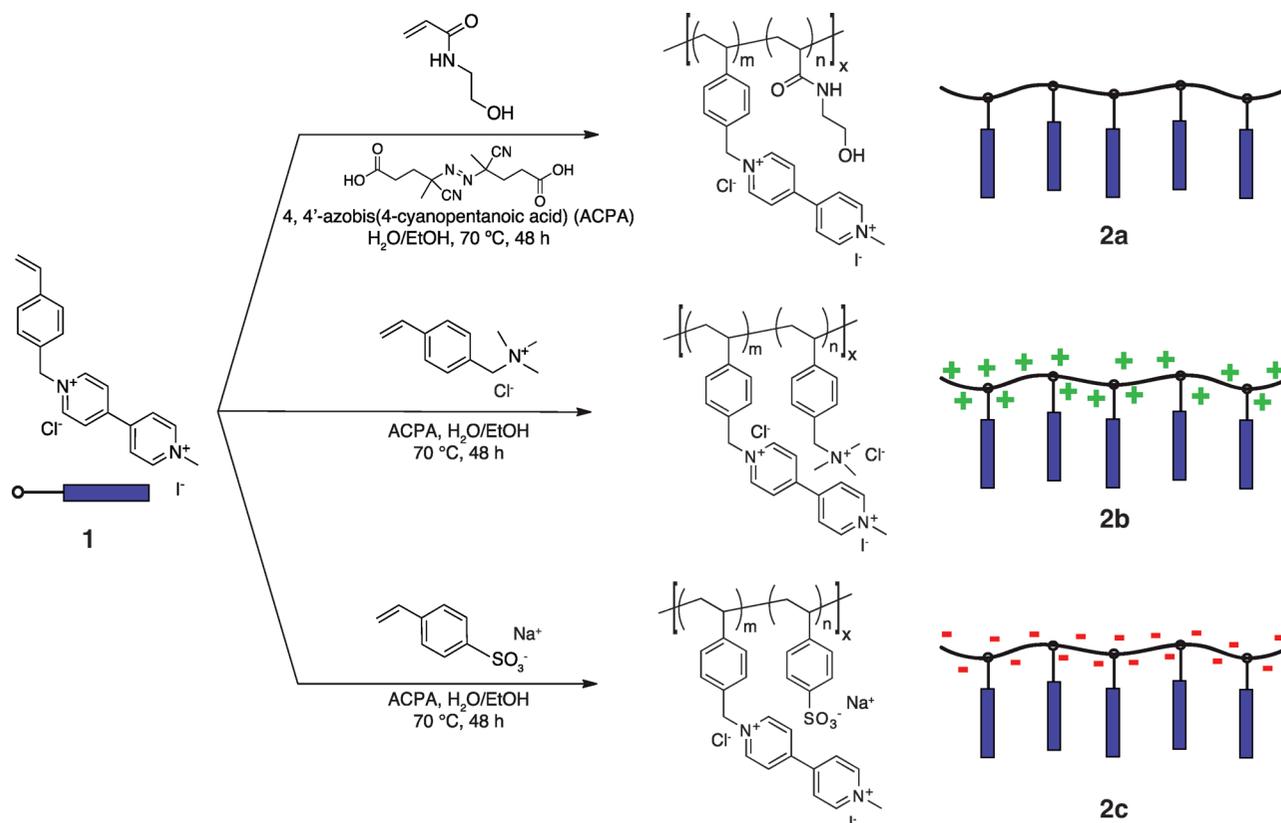
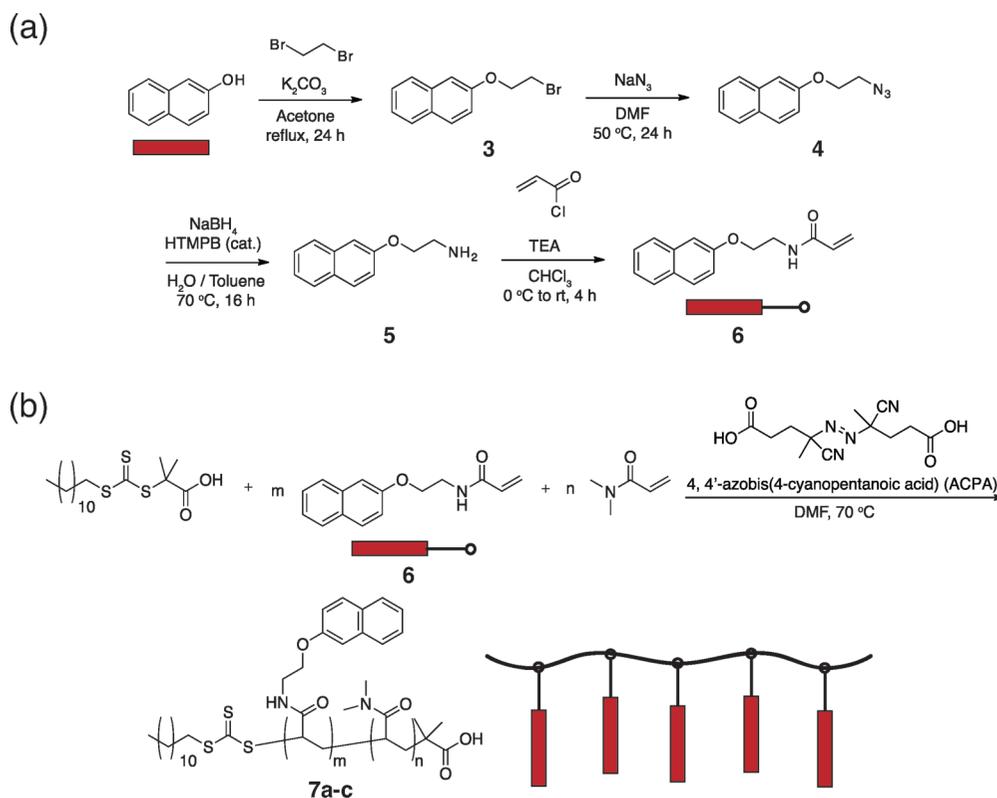
(39) Moad, G.; Rizzardo, E.; Thang, S. *Acc. Chem. Res.* **2008**, *41*, 1133–1142.

(40) Ogoshi, T.; Masuda, K.; Yamagishi, T.-A.; Nakamoto, Y. *Macromolecules* **2009**, *42*, 8003–8005.

(41) Leoni, A.; Franco, S.; Saini, G. *Makromol. Chem.* **1973**, *165*, 97–104.

(42) Saini, G.; Leoni, A.; Franco, S. *Makromol. Chem.* **1971**, *144*, 235.

(43) Saini, G.; Leoni, A.; Franco, S. *Makromol. Chem.* **1971**, *146*, 165.

Scheme 1. Synthetic Scheme for Preparation of MV-Functional Polymers **2a–c**^a**Scheme 2.** Synthetic Scheme for the Preparation of (a) Np-Functional Monomer **6** and (b) Np-Functional Polymers **7a–c**

comonomer adopts a semirigid rod conformation in solution as a result of charge–charge repulsion along the polymer backbone. The effect of this rigidity on the overall material

properties of the resulting gels and the effects of the differing ionic nature on 1:1:1 ternary complex formation and stability were investigated (*vide infra*).

Table 1. Functional Polymers Used To Prepare Supramolecular Hydrogels

Polymer	Functionality ^a (%)	M _n (kDa)	PDI
2a	10.1	27.4 ^b	1.53 ^b
2b	10.0	37.1 ^b	2.42 ^b
2c	9.8	26.8 ^b	2.09 ^b
7a	4.3	10.1 ^c	1.11 ^c
7b	10.1	10.1 ^c	1.12 ^c
7c	4.6	21.8 ^c	1.15 ^c

^a Determined by ¹H NMR. ^b Determined by GPC using H₂O as eluent. ^c Determined by GPC using DMF as eluent.

For the preparation of second-guest functional copolymers an Np-functional acrylamide monomer was designed for facile copolymerization with various acrylamide comonomers yielding nonionic, water-soluble polymers. Starting with 2-naphthol, Np-functional acrylamide monomer (NpAM) **6** was prepared after several high yielding steps (Scheme 2a). 2-Naphthol could be treated with a large excess of 1,2-dibromoethane in the presence of potassium carbonate to yield a primary bromo-functional naphthoxy moiety **3**. Conversion of the bromine with sodium azide and subsequent sodium borohydride reduction under phase transfer conditions adopted from a literature method by Rolla⁴⁴ gave the amine-functional naphthoxy moiety **5**. Preparation of naphthoxy-acrylamide monomer **6** was accomplished with acryloyl chloride in the presence of triethylamine under standard amide coupling conditions.

Reversible addition–fragmentation chain transfer (RAFT) polymerization was then used for the preparation of several multivalent, Np-functional copolymers with a well-known trithiocarbonate-based chain transfer agent (CTA) 2-(dodecanethiocarbonothioylthio)-2-methylpropanoic acid (DDMAT)⁴⁵ using standard RAFT conditions in DMF (Scheme 2b). DDMAT was used as it successfully mediates the polymerization of a wide variety of monomers (styrenics, (meth)acrylates, and (meth)acrylamides) in a variety of solvent conditions with high control over molecular weight and yielding low polydispersities (PDI). A series of polymers **7a–c** with varying molecular weights ranging from 10 to 22 kDa and loadings of functional NpAM monomer **6** ranging from 5 to 10% (Table 1) were prepared. A copolymer bearing a 20% loading of NpAM was synthesized; however, this polymer was not water-soluble. ¹H NMR analysis verified retention of the targeted loading of the functional monomer and overall molecular weight by comparing resonances resulting from the naphthoxy moiety, the methyl groups from the DMA comonomer, and the methylene in the α -position relative to the trithiocarbonate end group retained in the final polymers. GPC analysis of **7a–c** displayed that an exact overlay existed with both refractive index and UV–vis detectors (272 and 312 nm), demonstrating that each polymer bears both Np moieties (272 nm) and the trithiocarbonate (312 nm) from the RAFT CTA. While the examples shown have very specific structures, the use of free radical polymerization techniques provides a versatile and general method allowing for the incorporation of many other monomers or additional functionalities.

Self-Assembly of Multivalent Polymers. Isothermal titration calorimetry (ITC) is a powerful physical technique for measuring solution binding thermodynamics and stoichiometry and has been utilized previously to measure K_a values in CB[8]

Table 2. Thermodynamic Data for Second Guest Binding of Functional Polymers

Entry	MV	Np	K_a^a	ΔG^b (kcal/mol)	ΔH^c (kcal/mol)	$-\Delta S^c$ (kcal/mol)
1	2a	8	$8.8 (\pm 0.5) \times 10^4$	-6.7 ± 0.1	-13.3 ± 0.2	6.6 ± 0.2
2	2a	7a	$9.3 (\pm 0.5) \times 10^4$	-6.8 ± 0.1	-12.2 ± 0.2	5.4 ± 0.2
3	2a	7b	$1.5 (\pm 0.5) \times 10^5$	-7.0 ± 0.1	-8.8 ± 0.2	1.8 ± 0.2
4	2b	8	$7.0 (\pm 0.5) \times 10^4$	-6.6 ± 0.1	-9.6 ± 0.2	3.0 ± 0.2
5	2b	7a	$7.6 (\pm 0.5) \times 10^4$	-6.7 ± 0.1	-9.4 ± 0.2	2.7 ± 0.2
6	2b	7b	$8.0 (\pm 0.5) \times 10^4$	-6.7 ± 0.1	-8.7 ± 0.2	2.0 ± 0.2

^a Mean values measured from at least three ITC experiments at 25 °C in 10 mM PBS buffer at pH 7.0. ^b Gibbs free energy values calculated from K_a values. ^c Entropic contributions to ΔG calculated from K_a and ΔH values.

host–guest systems.^{35,37,46–48} With a range of multivalent polymers in hand the quantitative investigation of their respective binding thermodynamic parameters was carried out utilizing ITC. It was previously reported that no substantial decrease in the association equilibrium constant was observed for second-guests when attached at the end of a poly(ethylene glycol) chain.^{17,36} Our system contains both first and second guests pendant to a polymer backbone which could potentially increase the steric hindrance imposed on ternary complex formation with CB[8]. Additionally, the polymer backbones themselves could interact with (un)complexed CB[8] in a variety of ways. Therefore, ITC was used to determine the affinity of complexation, and Table 2 displays the complete thermodynamic data for second-guest binding based on the concentration of functional units (i.e., not polymer concentration), excluding anionic MV-functional polymer **2c** as it was unable to solubilize CB[8] sufficiently to perform the ITC measurements (*vide infra*). In order to identify the effect on binding stemming from both steric hindrance and the explicit structure of the polymeric backbones, ITC measurements were carried out on MV-functional polymers **2a–b** with both a monovalent small molecule **8** (2-naphthoxy functionalized with a triethylene glycol unit, NpTEG, see Supporting Information) and Np polymers **7a–b** in the presence of CB[8].

The ITC measurements highlighted in Table 2 showed that no significant difference in thermodynamic properties were observed between binding of either the monovalent small molecule **8** (entries 1 and 4) or the multivalent Np polymers **7a–b** (entries 2, 3, 5, and 6) to the multivalent MV polymers **2a–b** in the presence of CB[8]. Both MV polymers **2a–b** exhibited almost equivalent association constants and binding energies (Table 2) with all Np-functional materials tested, despite their structural differences. Likewise, there was no significant difference in association strengths observed for the two Np polymers **7a** and **7b**, despite **7b** bearing twice as many Np units per chain. These measurements identified that neither the added steric hindrance present around the Np moieties pendant from the polymer scaffold nor the loading of the functional monomer within that scaffold significantly affects binding strength.

Additionally, in the case of polymer–polymer binding, the multivalent binding interactions are noncooperative, i.e. the strength of each binding interaction is independent of all others.

(46) Rajgariah, P.; Urbach, A. R. *J. Inclusion Phenom. Macrocyclic Chem.* **2008**, *62*, 251–254.

(47) Bush, M.; Bouley, N.; Urbach, A. *J. Am. Chem. Soc.* **2005**, *127*, 14511–14517.

(48) Heitmann, L. M.; Taylor, A. B.; Hart, P. J.; Urbach, A. R. *J. Am. Chem. Soc.* **2006**, *128*, 12574–12581.

(44) Rolla, F. *J. Org. Chem.* **1982**, *47*, 4327–4329.

(45) Skey, J.; O'Reilly, R. *Chem. Commun.* **2008**, *35*, 4183–4185.

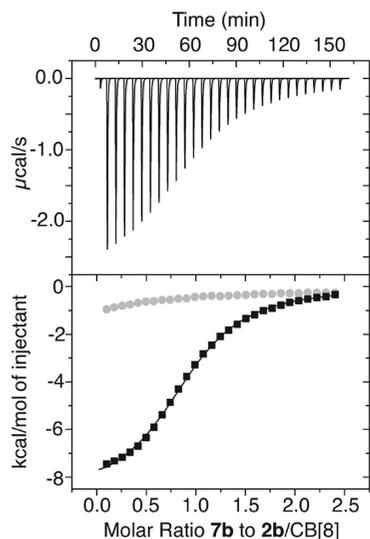


Figure 3. ITC data for the binding of **7b** to **2b**/CB[8] at 25 °C in 10 mM PBS buffer at pH 7.0. **7b** was titrated at 1 mM into a 0.1 mM solution of **2b**/CB[8]. The top plot displays the power applied as a function of time. The bottom plot displays integrated enthalpy values as a function of the molar ratio of **7b** titrated into **2b**/CB[8] (black squares) and 10 mM PBS buffer (gray dots).

Figure 3 displays the ITC data for the titration of **7b** into a buffered solution of **2b**/CB[8] and shows an isotherm that fits extremely well to a one-set-of-sites binding model and which has an inflection point at the 1:1 molar ratio of **7b** to **2b**/CB[8]. The presence of the inflection point at perfect 1:1 stoichiometry verifies that all Np and MV units are accessible and take part in binding interactions. These observations further verify that modern free radical polymerization techniques provide excellent control over polymer structure. The observed noncooperativity mentioned above is in contrast to a previous report by Urbach et al.³⁷ regarding the formation of multivalent oligopeptide assemblies with CB[8]. This disparity is likely on account of the highly variable nature and substantially longer average spacing between functional monomers in our random copolymers when compared with the well-defined aforementioned oligopeptides. It is the random and long-range spacing of functional monomers along the polymer scaffold that allows for the formation of large, cross-linked aggregates and networks instead of only dimers arising from the perfectly matched multivalent species reported by Urbach and co-workers.

Preparation of Supramolecular Hydrogels. Preparation of solutions of polymers from the various mixtures possible between **2a–c** and **7a–c** identified a large dependence of qualitative hydrogel properties on the ionic nature of the comonomer present in **2a–c**. The neutral variant **2a** was observed to form hydrogels with **7b**, although on account of the flexible nature of the backbone these materials exhibited a high concentration dependence. This mixture yielded supramolecular hydrogels only above 6 wt % with a 10% cross-link density through addition of 1 mol equiv of CB[8] with respect to MV and Np functional groups (i.e., 1 eq \times 10% functional monomer = 10% cross-link density). This sample is denoted **2a/7b/CB[8]_{10%}** where the percentage associated with CB[8] is the cross-link density of the network.

In comparison, the mixture of **7b** and cationic **2b** yielded the most promising hydrogel with high viscosity at 5 wt % in water and only requiring a 5% cross-link density through addition of 0.5 equiv of CB[8] with respect to MV and Np

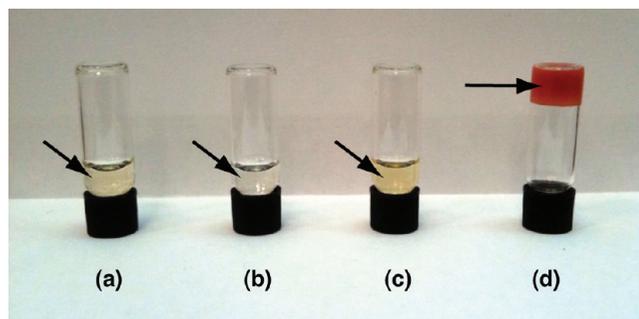


Figure 4. Inverted vial tests of (a) **2b**, (b) **7b**, (c) 1:1 mixture of **2b** and **7b**, and (d) 1:1 mixture of **2b** and **7b** upon addition of 0.5 mol equiv (i.e., 5% cross-linking) of CB[8] (denoted **2b/7b/CB[8]_{5%}**).

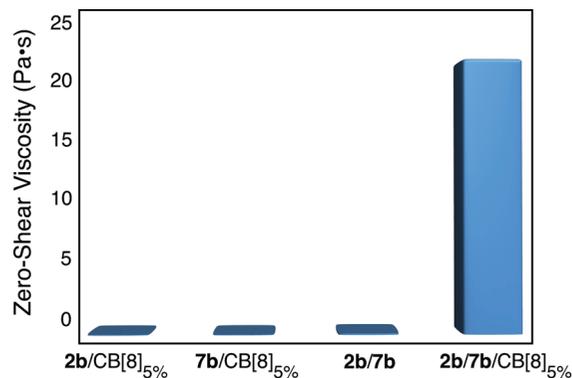


Figure 5. Column plot displaying quantitative zero-shear viscosities of the various component mixtures identifying that only the mixture of both types of functional polymers and CB[8] yields appreciable increases in viscosity.

functional groups (**2b/7b/CB[8]_{5%}**). The rigidity of **2b** on account of charge–charge repulsion along the polymer backbone contributed greatly to the overall viscosity of the supramolecular hydrogel, overcoming the slightly decreased association constant when compared with **2a**. Solutions of **2b**, **7b**, and a 1:1 (MV: Np) mixture of **2b** and **7b** were prepared and are displayed in Figure 4. In inverted vial tests of these solutions, no clear increase in solution viscosity indicating an increase in apparent molecular weight was observed, clearly demonstrating negligible interaction between the polymeric species themselves when dissolved in water at 5 wt %. As the MV dication moiety is colored, the corresponding functional copolymer **2b** is colored and the mixture of **2b** and **7b** bears the same light color of **2b** alone (Figure 4a and Figure 4c, respectively). Upon addition of CB[8] to the polymeric solution of **2b** and **7b** a brightly red colored, supramolecular hydrogel is formed (Figure 4d). This mixture contained 0.5 mol equiv of CB[8], leading to 5% cross-linking in the system, and is denoted **2b/7b/CB[8]_{5%}**. Additionally, quantitative zero-shear viscosities, shown in Figure 5, of the various component mixtures possible from **2b**, **7b**, and CB[8] clearly demonstrate that only the mixture of all three components together yields an appreciable increase in viscosity while all other mixtures lead to negligible increases over that of native water ($\eta_0 = 1 \times 10^{-3}$ Pa·s).

The high association between functional polymers upon ternary complexation with the supramolecular ‘handcuff’ CB[8] promotes dramatic increases in solution viscosity through 3D network formation. The bright red color is characteristic of the formation of a charge-transfer complex between the electron-poor MV and the electron-rich Np moieties within the cavity of the host molecule.^{35,37} This provides strong evidence that

Table 3. Rheological Characterization of Supramolecular Hydrogels

Entry	MV Polymer	Np Polymer	% Cross-linking ^a	Concn (wt %)	Viscosity (Pa·s) ^b
1	2a	7b	5	6.6	8.7
2	2b	7b	5	5	21
3	2c	7b	5	6.6	0.061
4	2b	7a	5	5	5.4
5	2b	7c	5	5	19

^a % Cross-linking is the % of monomer units participating in cross-link formation and is determined by the molar equivalent addition of CB[8]; therefore 5% cross-linking is achieved *via* addition of 0.5 equiv of CB[8] relative to functional monomer incorporation. ^b Zero-shear viscosity determined by steady shear rate sweep performed at 25 °C.

the 1:1:1 CB[8] ternary complex is formed and is responsible for 3D network formation from interchain complexation and commensurate increases in viscosity resulting in hydrogel formation.

In contrast, the negatively charged styrene sulfonate copolymer **2c** did not form hydrogels in the presence of CB[8] and **7b**, and the characteristic red color was only faintly observed. For this particular case, only a portion of the CB[8] added to the solution dissolved, identifying that the negative backbone, although semirigid, has detrimental interactions with the CB[8] host molecule upon complexation with the pendant MV moieties, decreasing the propensity for ternary complex formation and providing no increase in solution viscosity.

Control experiments were performed using smaller cucurbit[*n*]uril analogues, CB[6] and CB[7], which resulted in no increase in the viscosity of the polymeric solution of **2b** and **7b**. CB[7] is capable of full encapsulation of one MV moiety but not a second guest while CB[6] only binds MV partially in the portal region;^{29,49} therefore the 1:1:1 ternary complex cannot be formed in either case (i.e., no cross-linking is possible), providing support for our molecular picture of cross-linking *via* ternary complexation with the CB[8].

Rheological Characterization of Supramolecular Hydrogels. The successful design and preparation of supramolecular hydrogels affords the opportunity to employ complementary characterization techniques for these materials such as rheological studies which cannot be used for small molecule analogues of the supramolecular complexes. In order to probe the molecular dynamics of the reversible supramolecular hydrogels as well as quantify their mechanical properties rheological characterization was performed. Rheological analysis was carried out on supramolecular hydrogels prepared from the 1:1 mixture of each of the series of MV-functional polymers **2a–c** and Np-functional polymer **7b** with 0.5 mol equiv of CB[8] (relative to functional units yielding **2a–c/7b/CB[8]_{5%}**) corresponding to a 5% cross-link density in the networks. Quantitative zero-shear viscosities clearly verify the qualitative observations mentioned previously as hydrogels prepared with the cationic MV polymer **2b** exhibit much greater viscosities than either the neutral or anionic variants, even at lower concentrations (Table 3, entry 2 compared to entries 1 and 3). Additionally, supramolecular hydrogels prepared from the 1:1 mixture of MV-functional polymer **2b** and the remaining polymers in the series of Np-functional polymers (**7a** and **7c**, Table 3 entries 4 and 5, respectively) with 0.5 mol equiv of CB[8] (relative to functional

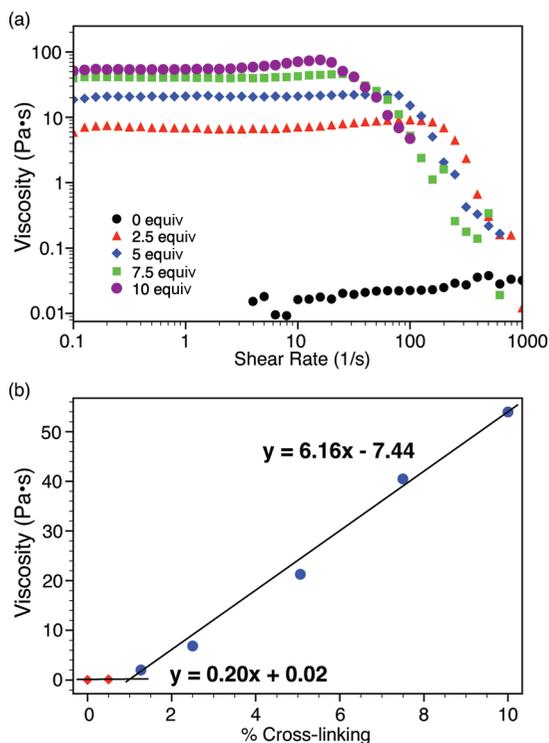


Figure 6. Rheological analysis of the 1:1 mixture of **2b** and **7b** with increasing cross-link densities from 0 to 10%. (a) Steady shear measurements and (b) zero-shear viscosity as a function of the % cross-linking in the supramolecular hydrogel determined by addition of CB[8] demonstrating the ‘gel point’ of the supramolecular network.

units yielding **2b/7a/CB[8]_{5%}** or **2b/7c/CB[8]_{5%}**) were characterized. As polymers **7a** and **7c** both have lower concentrations of Np functionality (5% functional monomer), the overall viscosities were lower when compared to **7b** as the concentration of ternary complexes was lower in the network. The 21.8 kDa polymer **7c** also exhibited increased viscosity over **7a** as the polymer contains twice as many cross-links per chain compared with **7a** (9.2 and 4.3, respectively) and is twice the molecular weight (21.8 and 10.1 kDa, respectively). These results clearly indicate that both the density of cross-links and polymer molecular weight affect the material properties.

As the mixture of cationic polymer **2b** and **7b** with CB[8] (**2b/7b/CB[8]_{5%}**) yielded the supramolecular hydrogels with the greatest viscosity, further rheological analysis was performed at 5 wt % in water with variable amounts of CB[8]. Steady shear analysis revealed dramatic increases ($>10^3$) in viscosity upon addition of CB[8] (Figure 6a) on account of 3D network formation. The viscosities of the 3D networks range between 5 and 55 Pa·s and increase linearly with the cross-link density (and therefore with CB[8] concentration) from 2.5% to 10% (Figure 6b). These viscosities between 10 and 100 Pa·s place our materials uniquely in a viscosity region for excellent processability. Additionally, our system seems to have several regions of rate dependent viscosity: Newtonian, shear-thickening and dramatically shear-thinning. Craig et al.⁵⁰ have recently noted similar behavior in a related polymeric organogel as being dominated by shear-induced changes in microstructure, where the number of elastically active chains increases with shear as *intramolecular* rings are converted to *intermolecular* cross-links.

(49) Kim, H.; Jeon, W.; Ko, Y.; Kim, K. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5007–5011.

(50) Xu, D.; Hawk, L. L.; Loveless, D. M.; Jeon, S. L.; Craig, S. L. *Macromolecules* **2010**, *43*, 3556–3565.

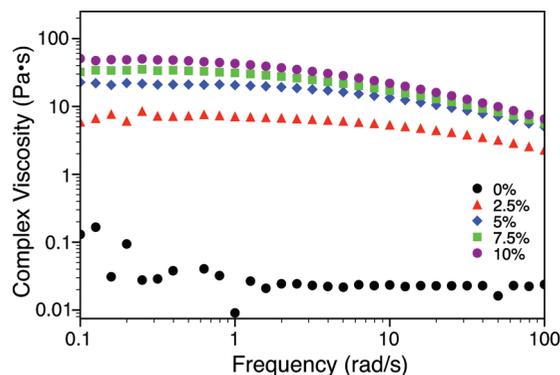


Figure 7. Complex viscosity plot obtained from dynamic oscillatory rheology at 10% strain of the 1:1 mixture of **2b** and **7b** with increasing cross-link densities from 0 to 10%.

As both the system described by Craig et al. and our system feature dynamic cross-links, it is reasonably inferred that our system is similarly capable of reorganization upon mechanical deformation. A plot of the zero-shear viscosity (η_0) versus the % cross-linking (Figure 6b) clearly demonstrated an inflection point characterizable as the ‘gel point’ where the cross-link density is great enough to induce full network formation. The ‘gel point’ was determined to be 1.25% (0.125 equiv of CB[8] relative to functional monomer) for the 1:1 mixture of **2b** and **7b** at 5 wt % in water.

Oscillatory rheological analysis also provided insight into dynamic mechanical properties of the supramolecular hydrogels. Figure 7 clearly demonstrates large increases in complex viscosity ($>10^3$) upon addition of CB[8] (2.5% cross-link density, just above the gel point). The complex viscosity continues to increase as more CB[8] is added (up to 10% cross-link density). It should be noted here that our system clearly does not follow the Cox–Merz rule, an empirical rule stating that the viscosity from steady shear measurements in hertz (Figure 6) should overlay the complex viscosity from the dynamic frequency sweep in rad/s (Figure 7). The dynamic frequency sweep identifies shear thinning behavior while the steady shear measurements demonstrate much more complicated rate-dependent behavior, as mentioned above. This corroborates the explanation for the observed rate dependent viscosity given above as shear can induce reorganization of the network structure through deformation of the material, while dynamic oscillatory measurements leave the network intact.

The dynamic measurements provide excellent insight into dynamic mechanical properties for viscoelastic materials, which contain both an elastic and a viscous response to mechanical perturbation. The elastic component, G' (storage modulus), is a measure of the energy stored in the active network after perturbation, while the viscous component, G'' (loss modulus), is a complementary measure of the energy lost through dissipated heat or relaxations in material. A simple representation of viscoelasticity in a material is the single mode Maxwell model that is typically used to describe viscous materials with some elastic response and can be described by a single relaxation rate β . The frequency dependencies of G' and G'' according to the single mode Maxwell model are as follows:

$$G' = G_0(\omega/\beta)^2/(1 + (\omega/\beta)^2) \quad (1)$$

$$G'' = G_0(\omega/\beta)/(1 + (\omega/\beta)^2) \quad (2)$$

where the bulk relaxation rate β is found from the crossover frequency of G' and G'' and the plateau modulus G_0 is found from

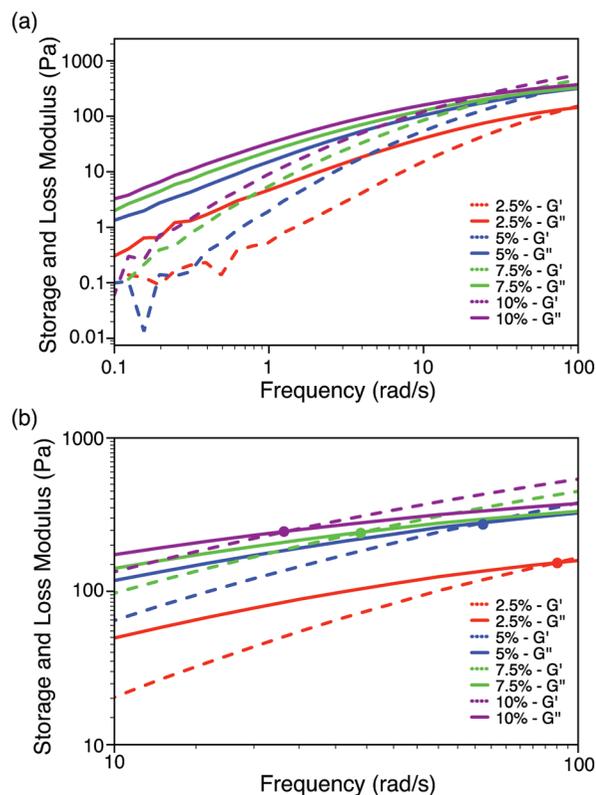


Figure 8. (a) Storage (G') and loss (G'') modulus of supramolecular hydrogels obtained from dynamic oscillatory rheology at 10% strain of the 1:1 mixture of **2b** and **7b** with increasing cross-link densities from 0 to 10%. (b) Zoom displaying decrease in G' and G'' crossover frequency β .

the plateau of G' . According to our molecular picture, the reversibly cross-linked 3D network responds to stress applied by the rheometer (oscillatory perturbations) by relaxing back to equilibrium at a rate β . At very slow oscillations ($\omega \ll \beta$) the viscous component G'' dominates as the reversible cross-links dissociate faster than the experimental time scale, demonstrating that they are not active cross-links capable of responding to the deformation energy. Conversely, at very fast oscillations ($\omega \gg \beta$) the elastic component G' dominates as the reversible cross-links are active on this timescale and capable of responding to the deformation energy.

Our hydrogel materials are viscoelastic, demonstrated in Figure 8, on account of the dynamic nature of the ternary complexation with CB[8]. These materials are rubbery (elastic) at shorter time scales (i.e., $\omega \gg \beta$) as the elastic component dominates, while they are viscous and flow at longer timescales (i.e., $\omega \ll \beta$) as the viscous component dominates. In the case of **2b/7b/CB[8]**, β decreases upon addition of CB[8] from 562 to 149 Hz between 2.5% and 10% cross-link density, demonstrating that the storage modulus of the supramolecular hydrogel has an increasingly important role in the system rheology as the cross-link density increases upon addition of CB[8]. Increasing CB[8] concentration, therefore, correlates to a greater number of active cross-links present in the supramolecular network, inducing faster relaxation of the network after oscillatory perturbation (i.e., greater elasticity). Additionally, the plateau modulus increases proportionally with CB[8] concentration from 350 to 600 pascals (Pa). This material therefore exhibits intermediate mechanical properties (i.e., plateau modulus ≈ 10 –1000 Pa) and provides an excellent complement to the polymer–clay hybrid hydrogel system recently reported by Aida and co-workers, which exhibits a much higher mechanical strength (plateau modulus $>10^4$ – 10^6 Pa).¹⁶ These observations

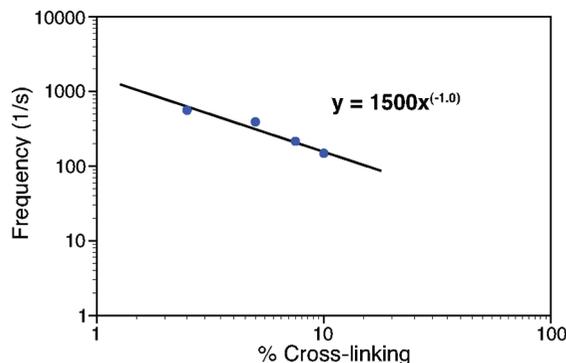


Figure 9. Network relaxation rate β (the G' and G'' crossover frequency in hertz) as a function of the % cross-linking in the supramolecular hydrogel formed from the 1:1 mixture of **2b** and **7b** with CB[8].

further confirm that the observed increase in viscosity is due to cross-linking through 1:1:1 heteroternary complexation.

Looking further into the oscillatory rheology of the system, β changes as a function of cross-link density according to an inverse power law with a dependence of $(\% \text{ cross-link})^{-1}$ (Figure 9), consistent with theoretical models for supramolecular transient networks.⁵¹ According to the seminal studies by Craig et al.^{52,53} the kinetics of molecular cross-links in supramolecular systems are of greater importance than binding thermodynamics in determining the bulk viscoelastic properties of the material. It has been demonstrated that extrapolation of the relaxation rate plot back to the cross-link density at the gel point yielded the ‘apparent’ intrinsic relaxation rate (β_{int}) of the network (i.e., the dissociation rate of supramolecular cross-links), found to be equivalent to the k_d determined from corollary NMR studies of the small-molecule supramolecular motif.⁵³ Applying the same method by using the cross-link density at the gel point determined from viscosity titrations (1.25%), extrapolation of the plot in Figure 9 yields a dissociation rate constant of the ternary complex $k_d = 1200 \text{ s}^{-1}$.

This k_d value is remarkably high when considering the intrinsic motion limitations of the ternary complex within the 3D cross-linked network. The implication of such a high k_d when considering the solution K_a value for second guest binding from ITC measurements (Table 3, entry 6) is an association rate constant ($k_a = 9.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) which is approaching the diffusion limit (Figure 2b). Studies are currently underway to further analyze binding dynamics for CB[8] ternary complexation both with small molecules and with polymeric materials. While the association rate constant obtained using the method developed by Craig et al. is high, it is a reasonable value as k_d is expected to be greater than 200 s^{-1} (limit of the NMR) due to the appearance of singular, broad peaks observed in previously published NMR studies.¹⁷ These studies clearly demonstrate fast exchange of the second guest for MV/Np/CB[8] ternary complexes in both small molecule and polymeric systems. These observations offer important insight into the binding mechanism of CB[8] ternary complexation as the primary driving force for complexation is an extremely high association rate (as opposed to a very low dissociation rate), yielding dynamically cross-linked materials with potentially

ultrafast network recovery after destruction of the existing network *via* shear stress, etc. Furthermore, it is worth noting that while dissociation rate constants have been measured and reported for CB[6]^{54–58} and CB[7]^{57,59} 1:1 complexes with (di)cationic guests, no report on the binding dynamics of a CB[8] ternary complex has appeared in the literature to date. In both CB[6] and CB[7] complexes, the reported k_a and k_d values are much lower and can be measured by NMR, while in our system we are only measuring the rate constants for second guest binding which is largely driven by hydrophobic interactions and desolvation of the second guest.³⁵

Microstructure of Supramolecular Hydrogels. The microstructure of these supramolecular hydrogels (**2b/7b/CB[8]**) were investigated using scanning electron microscopy (SEM) after cryo-drying. The supramolecular networked systems retain the characteristic bright red color of the ternary complex charge-transfer band, identifying that the supramolecular network is still intact while in the solid state. Figure 10 shows SEM images of the 1:1 mixture of **1b** and **2b** at 5 wt % in water with increasing cross-link densities demonstrating that each of the hydrogels has a very uniform, highly ordered microstructure. As the cross-link density increases, the pore size within the polymeric matrix decreases from approximately 12 to 3 μm between 2.5% and 10% cross-linking, corroborating the rheological observations. The decrease in pore size with increasing cross-link density is consistent with typical covalent cross-linked hydrogels.

The hydrogel microstructure was also used as a platform to probe the hydrogel response to thermal stimuli. A sample of **2b/7b/CB[8]**_{2.5%} cross-linked with 0.25 mol equiv of CB[8] gave the hydrogel depicted on the left of Figure 11. SEM micrographs clearly demonstrate that the microstructure consists of large pores approximately equal in size to those described previously (12 μm) for the 2.5% cross-linked sample depicted in Figure 10d. Qualitative evidence for the thermal reversibility of this hydrogel is demonstrated with an inverted vial test. Upon heating, the hydrogel undergoes a gel-to-sol conversion and readily flows as the second guest K_a value decreases at increased temperatures. This conversion is completely reversible, and the hydrogel reforms upon cooling (Figure 11a). If more CB[8] is then added to the vial (up to a total of 1 mol equiv), heating of the gel and subsequent shaking allow for dissolution of the additional CB[8], yielding a hydrogel with 10% cross-linking upon cooling. This hydrogel, now formed with a higher cross-link density, remained fully thermally reversible. An immediate observation is that the red color of the hydrogel is much more intense on account of a higher concentration of ternary complexes within the network structure. This is consistent with observations made previously in CB[8] ternary complex systems.³⁷ Additionally, SEM micrographs identify a drastic change in the hydrogel microstructure as much smaller pore sizes are now measured which are consistent with those previously measured for a directly prepared sample of 10% cross-linking

(51) Jongschaap, R.; Wientjes, R.; Duits, M.; Mellema, J. *Macromolecules* **2001**, *34*, 1031–1038.

(52) Yount, W.; Loveless, D.; Craig, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2746–2748.

(53) Yount, W.; Loveless, D.; Craig, S. *J. Am. Chem. Soc.* **2005**, *127*, 14488–14496.

(54) Mukhopadhyay, P.; Zavalij, P. Y.; Isaacs, L. *J. Am. Chem. Soc.* **2006**, *128*, 14093–14102.

(55) Mock, W. L.; Shih, N. Y. *J. Org. Chem.* **1986**, *51*, 4440–4446.

(56) Mock, W. L.; Shih, N. Y. *J. Am. Chem. Soc.* **1989**, *111*, 2697–2699.

(57) Marquez, C.; Nau, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 3155–3160.

(58) Marquez, C.; Hudgins, R. R.; Nau, W. M. *J. Am. Chem. Soc.* **2004**, *126*, 5808–5816.

(59) Jeon, W.; Moon, K.; Park, S.; Chun, H.; Ko, Y.; Lee, J.; Lee, E.; Samal, S.; Selvapalam, N.; Rekharsky, M.; Sindelar, V.; Sobransingh, D.; Inoue, Y.; Kaifer, A.; Kim, K. *J. Am. Chem. Soc.* **2005**, *127*, 12984–12989.

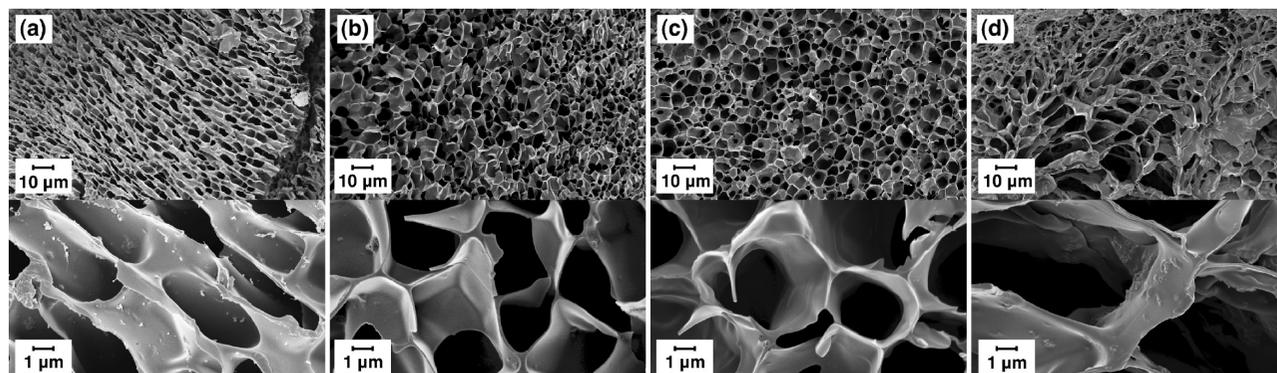


Figure 10. Scanning Electron Microscopy (SEM) images of the cryo-dried supramolecular hydrogels from **2b** and **7b** with decreasing cross-link densities from (a) 10%, (b) 7.5%, (c) 5%, and (d) 2.5%.

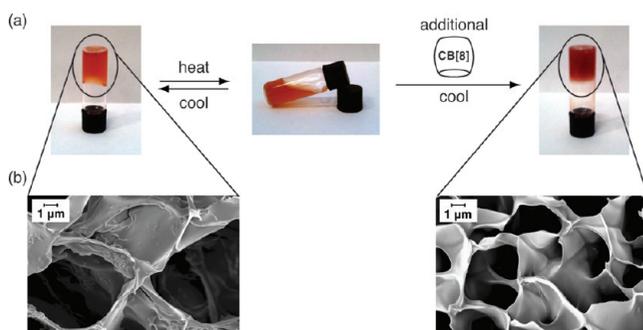


Figure 11. (a) Inverted vial test demonstrating thermal reversibility of the supramolecular hydrogel. (b) SEM images demonstrating network reversibility as further addition of CB[8] to a hydrogel of low cross-link density (2.5%) following heating elicits network restructuring as cross-link density increases (**2b/7b/CB[8]**_{2.5%} → **2b/7b/CB[8]**_{10%}).

(3–4 μm, Figure 10a). These observations verify that the hydrogels formed using CB[8] ternary complexation are thermally sensitive and fully reversible and that the material properties are easily modulated through the addition of CB[8].

Conclusion

In summary, we have demonstrated the preparation of a series of multivalent side-chain functional polymers bearing either a good first (viologen) or second (naphthoxy) guest using versatile free radical polymerization techniques. Additionally, these polymers have been used as a platform demonstrating that 1:1:1 ternary complexation mediated by the supramolecular host molecule CB[8] is a powerful and effective motif for the preparation of dynamic supramolecular hydrogels. The use of this strong and highly directional, stimuli-responsive supramolecular motif takes full advantage of a unique three-component binding mode inducing supramolecular cross-linking and large viscosity increases ($>10^3$). Characterization of the supramo-

lecular hydrogels indicates that the material properties and hydrogel pore sizes can be modulated with the amount of CB[8] added to the system. Moreover, rheological analysis allowed for the kinetics of CB[8] ternary complexation to be determined for the first time. The rates of second guest association and dissociation are undoubtedly important parameters to consider in the design of future CB[8]-containing systems that has only become characterizable using rheological analysis of these polymeric networked materials on account of time scale limitations of analytical techniques typically used. These materials exhibited intermediate mechanical properties (plateau modulus = 350–600 Pa and zero-shear viscosities = 5–55 Pa·s), placing them as a complement to existing supramolecular hydrogels and identifying their potential for use in industrial applications requiring this processing window. Additionally, these supramolecular hydrogels exhibited thermal reversibility and subsequent facile modulation of microstructure upon further addition of CB[8] and thermal treatment. This previously unexplored approach offers a versatile method for the preparation of sophisticated supramolecular hydrogels facilitating progress in the field of smart, self-healing materials, self-assembled hydrogels, and controlled solution viscosity.

Acknowledgment. The authors would like to acknowledge Dr. Simon Butler and Prof. Malcolm Mackley for their helpful discussions regarding rheological characterization. This work was supported in part by Schlumberger and the Walters-Kundert Trust.

Supporting Information Available: Experimental procedures and ^1H NMR, GPC, and ITC measurements can be found in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA106362W