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Multiresponsive Reversible Polymer Networks Based on Hydrogen Bonding and Metal Coordination

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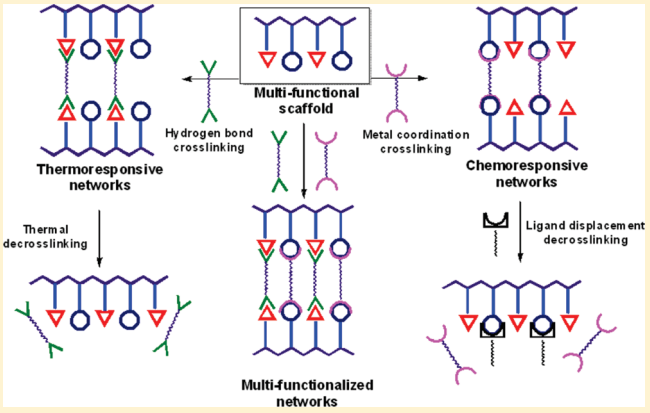
ABSTRACT: Side-chain-functionalized polymers containing hydrogen bonding and metal coordination sites have been synthesized using ring-opening metathesis polymerization. These polymers were cross-linked reversibly either selectively by using hydrogen bonding or metal coordination or simultaneously using both interactions through the addition of small molecule cross-linking agents. The hydrogen bonding motifs utilized for reversible cross-linking are based on cyanuric acid residues hydrogen bonded to 2,4-diaminotriazine-based cross-linking agents. The metal coordination motifs are based on palladated SCS pincer complexes coordinated to bispyridine cross-linking agents. By controlling the reversible cross-linking strategy, we were able to modulate (1) the rheology of the polymer networks from a free-flowing liquid to a highly elastic gel and vice versa and vary the dynamic moduli over 10 orders of magnitude and (2) the responsiveness of the networks to external stimuli such as temperature and ligand displacement agents. The hydrogen bonded cross-linking resulted in polymer networks that were thermally reversible whereas the metal coordinated cross-linked networks mainly showed chemoresponsive behavior. Since both interactions are fully orthogonal to each other, we successfully cross-linked the polymer using both interactions to obtain multiresponsive networks that exhibited both thermal and chemoresponsiveness. We were also able to selectively de-cross-link the hydrogen bonded cross-links of the multifunctionalized networks through competitive interactions at room temperature via the addition of a monotopic end-capping agent without affecting the metal coordinated cross-links. In contrast, the metal coordination could be de-cross-linked completely using a ligand displacement agent such as triphenylphosphine again without affecting the hydrogen bonded cross-links.



INTRODUCTION

Noncovalent interactions, especially molecular recognition processes, offer a highly reversible, functional, and tunable strategy to the traditional cross-linking of polymers based on covalent processes which are often unidirectional and irreversible.[1−13] Noncovalent cross-linking through molecular recognition processes involving interactions such as hydrogen bonding,[14−21] metal coordination,[9,22−26] and Coulombic interactions[27,28] also allows for the control and tailoring of the responsiveness of cross-linked networks to external stimuli such as temperature, solvent, and pH.[3,4,29,30,44] Examples include the use of metal coordination to create materials that are responsive to redox reactions and metal−ligand displacement agents[30−32] or the employment of hydrogen bonding interactions to create cross-linked polymer networks that are sensitive to temperature.[3,44] This tunability and responsiveness make noncovalently cross-linked polymers uniquely interesting for a range of applications such as self-repair,[12,33,34] highly controlled and functionalized materials,[21,35,36] and stimuli responsive materials.[37]

Noncovalently cross-linked materials reported in the literature use only a single molecular recognition motif, thereby limiting their responsiveness.[26,38−40,44] A multifunctional cross-linking strategy would allow for a single polymer to form unique multiresponsive materials. Noncovalently multifunctionalized cross-linked side-chain polymers offer a strategy toward this goal by creating multiresponsive cross-linked materials with a high degree of complexity. This strategy requires the employment of an orthogonal cross-linking strategy using more than one molecular recognition process. We have reported the synthesis of noncovalently functionalized polymers prepared from a single polymer backbone via directional self-assembly processes using a combination of metal coordination and hydrogen bonding interactions.[2,41,42] Herein, we report the use of our orthogonal noncovalent multifunctionalization strategy to synthesize reversibly

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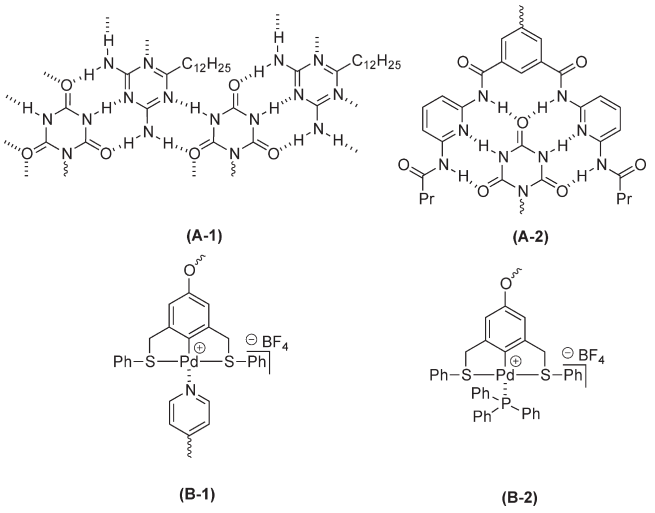


Figure 1. Self-assembly motifs employed in this study. Hydrogen bonding interactions: (A-1) multipoint hydrogen bonded array based on two- and three-point hydrogen bonded complexes between 2,4-diaminotriazine and cyanuric acid and (A-2) six-point hydrogen bonded complex between the Hamilton wedge and cyanuric acid. Metal coordination interaction: (B-1) pyridine-SCS Pd metal coordinated complex and (B-2) triphenylphosphine-SCS Pd metal coordinated complex.

cross-linked materials. Our system allows for the selective de-cross-linking using either hydrogen bonding or metal coordination. As a result, these materials offer a high degree of control over the final material properties and ultimately the underlying strategy might be useful in designing tailor-made materials.

Our system is based on a terpolymer functionalized with cyanuric acid as the hydrogen bonding receptor moiety, palladated SCS pincer complexes for metal coordination, and a third inert spacer monomer to increase polymer solubility in nonpolar solvents. We have extensively studied both the cyanuric acid and palladated SCS pincer complex supramolecular motifs in functionalized polymer systems.[2,31,41−43] In this contribution, we report two distinct cross-linking schemes: cross-linking via hydrogen bonding interaction and/or metal coordination. Previously, we have reported that 2,4-diaminotriazine-functionalized cross-linking agents can reversibly cross-link cyanuric acid side-chain-functionalized polymers to form stable thermoresponsive polymer networks (Figure 1).[44] In addition to thermal reversibility at elevated temperatures, these networks could also be de-cross-linked at room temperature using a de-cross-linking agent that selectively displaced the hydrogen bonded cross-link to form a more stable hydrogen bonded complex (Figure 1). This de-cross-linking agent was based on *N*1,*N*3-bis(6-butyramidopyridin-2-yl)isophthalamide (often called Hamilton wedge) as it can undergo strong six hydrogen bonding with cyanuric acid ($K_a \sim 10^4-10^5$ M^{-1} in halogenated solvents at room temperature) while the hydrogen bonding between cyanuric acid and 2,4-diaminotriazine is only a weaker, three-point interaction.[44,45] We have also reported the use of metal coordination to reversibly cross-link polymers using bispyridine as a cross-linking agent for SCS palladated pincer functionalized side-chain polymers (Figure 1).[31] These metal cross-linked polymers were shown to be chemoresponsive as they could be de-cross-linked using triphenylphosphine as a ligand displacement agent (Figure 1).[31] In this report we utilize both of these reversible interactions to selectively as well as simultaneously cross-link multifunctionalized polymer scaffolds to give a family of multi-responsive, reversible polymer networks whose mechanical properties can be tuned ranging from free-flowing liquids to stable viscoelastic gels. As a result, these materials offer a high degree of control over the final material properties, allowing potentially for the design of tailor-made materials.

EXPERIMENTAL SECTION

General. All reagents were purchased either from Acros Organics, Aldrich, or Strem Chemicals and used without further purification unless otherwise noted. Grubbs' first-generation initiator was purified by filtration using benzene under an atmosphere of argon. Cyanuric acid monomer **2**,[43] spacer monomer **1**,[31] pincer monomer **3**,[46] dodecyl-2,4-diaminotriazine **4**,[47] and **6**[44] were synthesized according to literature procedures. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were taken using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Abbreviations used below in the description of materials synthesis include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), and unresolved multiplet (m). Gel permeation chromatography (GPC) analyses were carried out using a Shimadzu pump, a Shimadzu UV detector with tetrahydrofuran (THF) as the eluant, and a set n Polymer Standards columns (100, 1000, 100 000 Å linear mixed bed). The flow rate used for all the measurements was 1 mL/min. All GPC measurements were calibrated versus poly(styrene) standards and were carried out at room temperature. M_w, M_n, and PDI represent the weight-average molecular weight, number-average molecular weight, and the polydispersity index, respectively. Rheological measurements were carried out on an MCR300 controlled stress rheometer (Anton Paar), equipped with Peltier elements for temperature control and an evaporation blocker that enables measurements at elevated temperature in a cone−plate geometry (diameter 50 mm, angle 1°).[48] All measurements were carried out in oscillatory mode in order to probe the equilibrium structures of the polymer solutions.

Poly-123. Monomers **1** (3.6 g, 14.4 mmol), **2** (754 mg, 1.8 mmol), and **3** (1.39 g, 1.8 mmol) were dissolved in 30 mL of $CHCl_3$. A stock solution of Grubbs' first-generation initiator was prepared in $CHCl_3$, and an amount of the stock solution equaling 118 mg ([M]/[I] = 125:1) of the initiator was added to the monomer solution. The solution was stirred at room temperature, and the reaction was monitored by observing the olefinic signals of the monomer by ^{1}H NMR spectroscopy. Upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization, followed by prolonged drying at room temperature under high vacuum for 24 h to remove all the solvent. ^{1}H NMR (300 MHz CD_2Cl_2): δ = 7.80 (m, 4H, SPh), 7.40 (m, 6H, SPh), 6.56 (s, 2H, ArH), 5.50−5.07 (m, 6H, CH═CH), 4.55 (br s, 4H, CH_2S), 4.09−3.9 (m, 6H, CH_2O), 3.8−3.7 (m, 4H, CH_2O, CH_2N), 3.2−1.0 (m, 69H), 0.86 (t, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (400 MHz CD_2Cl_2): δ = 174.0, 156.7, 151.6, 150.3, 149.9, 148.8, 133.5, 132.7, 131.9, 131.0, 129.6, 108.9, 67.7, 64.0, 50.8, 49.8, 49.2, 47.5, 41.7, 38.3, 37.0, 35.9, 35.2, 34.6, 31.6, 29.2−28.2, 27.7, 26.7−25.8, 22.8, 22.4, 14.1. M_n = 29 000, M_w = 36 000, PDI = 1.24.

Hydrogen Bonding Cross-Linking Using 4. Poly-123 (190 mg, 0.06 mmol based on the hydrogen bonding functional groups along the polymer backbone) was dissolved in 1.72 g of 1-chloronaphthalene (10 wt %). Then 17 mg (0.06 mmol based on the hydrogen bonding units) of **4** was added to the sample, and the suspension was heated until a clear homogeneous solution was obtained, which quickly gelled when cooled to room temperature. The gel was then allowed to rest at room temperature for at least 12 h before rheological measurements were carried out.

Metal Coordinated Cross-Linking Using 5. Poly-123 (190 mg, 0.06 mmol based on the metal coordination functional groups along the

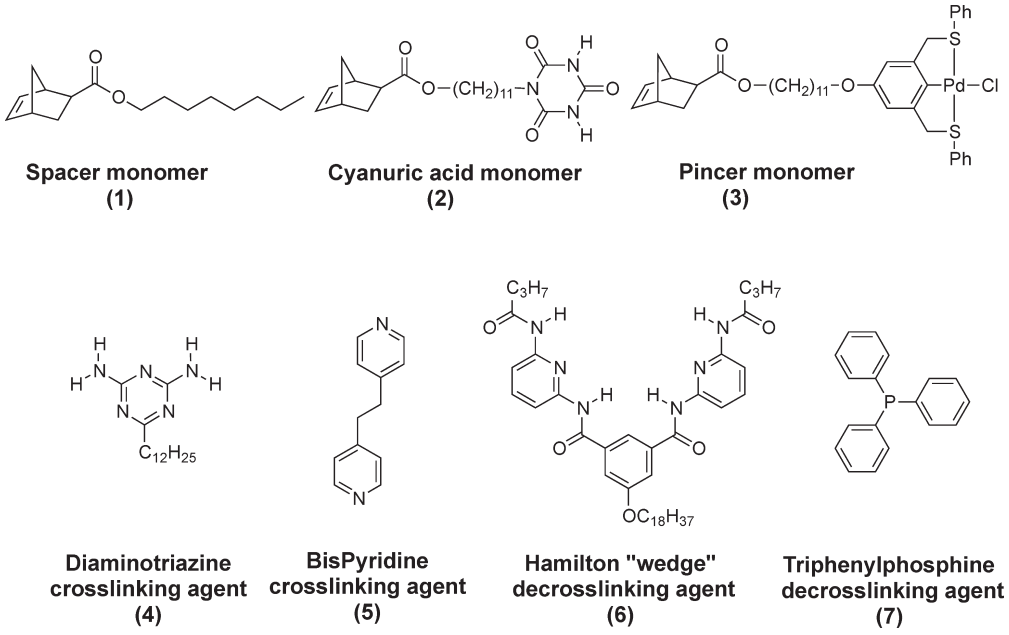


Figure 2. Monomers **1**−**3**, cross-linking agents **4** and **5**, and de-cross-linking agents **6** and **7** utilized in this study.

polymer backbone) was dissolved in 1.72 g of 1-chloronaphthalene (10 wt %). Then 6 mg (0.03 mmol based on the metal coordination units allowing for quantitative cross-linking) of **5** and 12 mg of silver tetrafluoroborate were added to the sample, and the mixture was stirred at 80 °C for at least 6 h. The sample was then allowed to rest at room temperature for 12 h before the rheological experiments were carried out. The sample gelled upon resting at room temperature after about 1−2 h.

Multifunctional Cross-Linking Using 4 and 5. Poly-**123** (190 mg, 0.06 mmol based on the metal coordination or the hydrogen bonding units along the polymer backbone) was dissolved in 1.72 g of 1-chloronaphthalene (10 wt %). Then 17 mg (0.06 mmol based on the hydrogen bonding units) of **4**, 6 mg (0.03 mmol based on the metal coordination sites allowing for quantitative cross-linking) of **5**, and 12 mg of silver tetrafluoroborate were added to the sample, and the mixture was stirred at 80 °C for at least 6 h. The samples gelled quickly upon resting at room temperature. The sample was then allowed to rest at room temperature for 12 h before the rheological experiments were carried out.

Multifunctional De-Cross-Linking Using 6 and 7. Poly-**123**-**45** (above sample in 1-chloronapthalene) was mixed with 46 mg (0.06 mmol based on the hydrogen bonding sites) of **6** and 16 mg (0.06 mmol based on the metal coordination sites allowing for quantitative de-cross-linking) of **7**, and the mixture was stirred at 80 °C for at least 6 h. The gel was gradually transformed to initially a viscous liquid, which after 2−3 h turned into a free-flowing liquid. The sample was then allowed to rest at room temperature for 12 h before the rheological experiments were carried out.

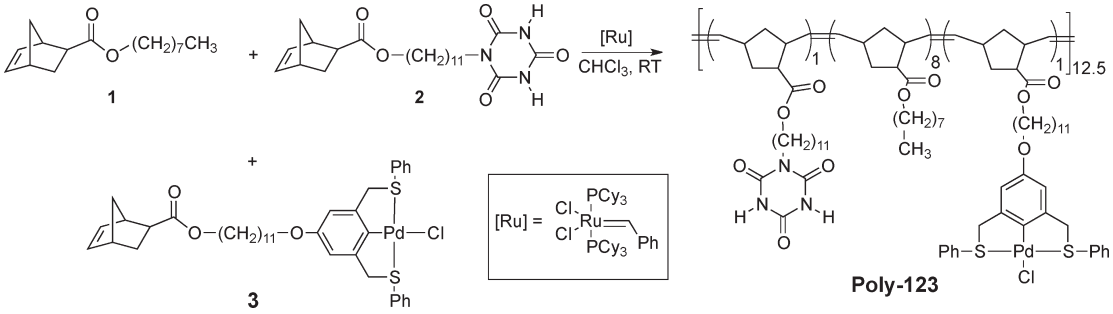
Rheology. The rheological testing protocol of all polymer solutions consisted of (1) a strain amplitude sweep at constant frequency (temperature 20 °C; strain amplitude $\gamma = 0.001-10$, angular frequency $\omega = 6.28$ rad/s) to confirm the linear viscoelastic regime, (2) a frequency sweep at constant strain amplitude (20 °C; $\gamma = 0.01$; $\omega = 0.1-100$ rad/s) to determine network viscoelasticity, the strain value was kept low to ensure that all the measurements were obtained in the linear viscoelastic regime, (3) a temperature sweep (20−80 °C; $\gamma = 0.1$; $\omega = 6.28$ rad/s) to characterize thermal stability, (4) a high-temperature frequency sweep at constant strain amplitude (80 °C; $\gamma = 0.1$; $\omega = 0.1-100$ rad/s), (5) temperature sweep (80−20 °C; $\gamma = 0.01$; $\omega = 6.28$ rad/s) to investigate thermal reversibility, and (6) a frequency sweep at constant strain amplitude after cooling down the sample from 80 °C (20 °C; $\gamma = 0.1$; $\omega = 0.1-100$ rad/s) to determine thermal recovery.

RESULTS AND DISCUSSION

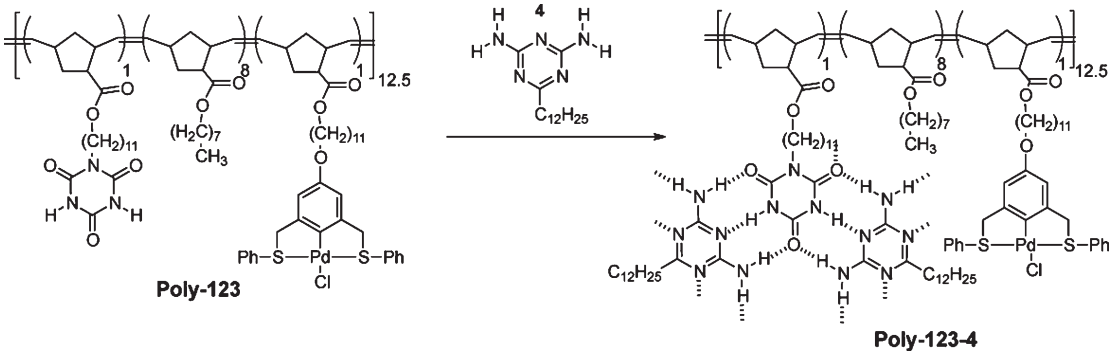
Figure 2 describes the norbornene monomers **1**−**3**, cross-linking agents **4** and **5**, and de-cross-linking agents **6** and **7**. Monomer **1** serves, after ROMP, as a diluent for the cyanuric acid monomer **2** and the pincer monomer **3** along the polymer backbone and increases the solubility of all copolymers in nonpolar solvents. The cross-linking agents and de-cross-linking agents are either commercial available as in the case of **5** and **7** or have been synthesized as reported in the literature (cross-linking/de-cross-linking agents **4**−**6**).[44] Hydrogen bonded cross-linking was carried out by employing **4**, whereas the metal coordinated cross-linking was carried out by the addition of **5** after activation of the SCS Pd complexes. De-cross-linking experiments were carried out using either **6** or **7**. All cross-linking and de-cross-linking experiments and the subsequent characterizations of the resulting cross-linked polymer networks were carried out in 1-chloronaphthalene using rheology.

Copolymerization. The polymerization behaviors of monomers **1**−**3** have been reported previously.[31,41,43,44] All monomers can be copolymerized in a random fashion via ROMP in chloroform at room temperature using Grubbs' first-generation initiator (Scheme 1). Complete monomer conversion was obtained within 3 h at room temperature for a monomer to initiator ratio of 125:1, which we have shown recently to be the optimal molecular weight for cross-linking studies in 1-chloronapthalene using rheometry.[44] The molar content of both **2** and **3** in the polymer was kept at 10% so that the polymer and the subsequent cross-linked networks are completely soluble in 1-chloronapthalene at room temperature and do not undergo phase separation. The terpolymer was characterized using gel permeation chromatography. The weight-average molecular weight was 36 000, and the number-average molecular weight was 29 000 with a polydispersity index of 1.24.

Scheme 1. Synthesis of Poly-123 via ROMP Using Grubbs' First-Generation Initiator



Scheme 2. Noncovalent Cross-Linking of Poly-123 Using 4 Resulting in the Formation of Multipoint Hydrogen Bonded Network Poly-123-4



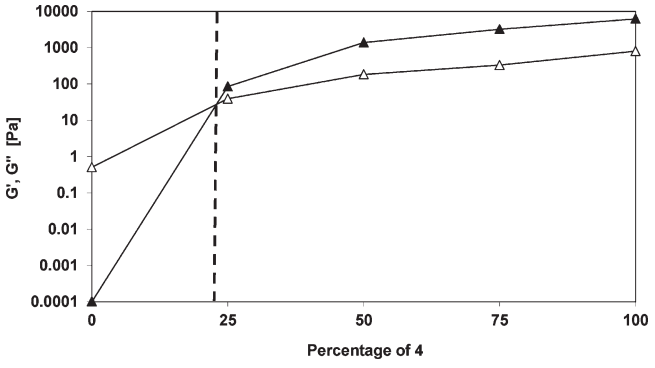


Figure 3. Plot of G' and G'' versus the amount of **4** for **Poly-123**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at a strain value of 0.1 and around an angular frequency of 6.28 rad/s. The concentration of **4** is defined relative to the molar concentration of cyanuric acid groups.

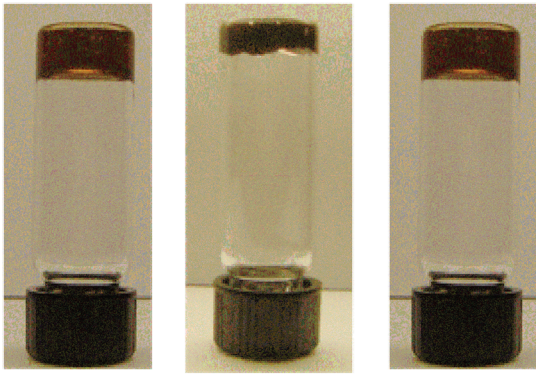


Figure 4. Pictures of inverted vials with (A) **Poly-123-4**, (B) **Poly-123-5**, and (C) **Poly-123-45** at room temperature. All samples were dissolved in 1-chloronaphthalene and prepared from 1:1 ratios of recognition units along the polymer backbone to the desired additives **4** and **5**. Pictures were taken 2 h after vial inversion at room temperature.

Cross-Linking via the Use of a Single Recognition Motif. Terpolymer **Poly-123** can be viewed as a multifunctional polymer scaffold that can be cross-linked through the addition of **4** causing cross-linking through the cyanuric acid groups and/or the addition of **5** resulting in cross-linking through the activated SCS pincer Pd centers. We initially investigated the hydrogen bonded cross-linking of **Poly-123** using **4** (Scheme 2). Previously, we reported that **4** forms stable, thermally responsive polymer networks with cyanuric acid-functionalized polymers via multipoint interchain hydrogen bonding interactions.[44]

In contrast to self-associative (or dimerizing) hydrogen bonded polymer networks, our polymer networks are based on complementary hydrogen bonding interactions.[31,44] Hence, the degree of cross-linking of these polymer networks can be manipulated easily by varying the amount of cross-linking agent added to the polymer scaffold.[44] We added varying concentrations of **4** (0% to 100% molar ratio of functional groups of the cross-linking agent to the cyanuric acid groups attached to the polymer backbone) to **Poly-123** and characterized the resulting networks **Poly-123-4**

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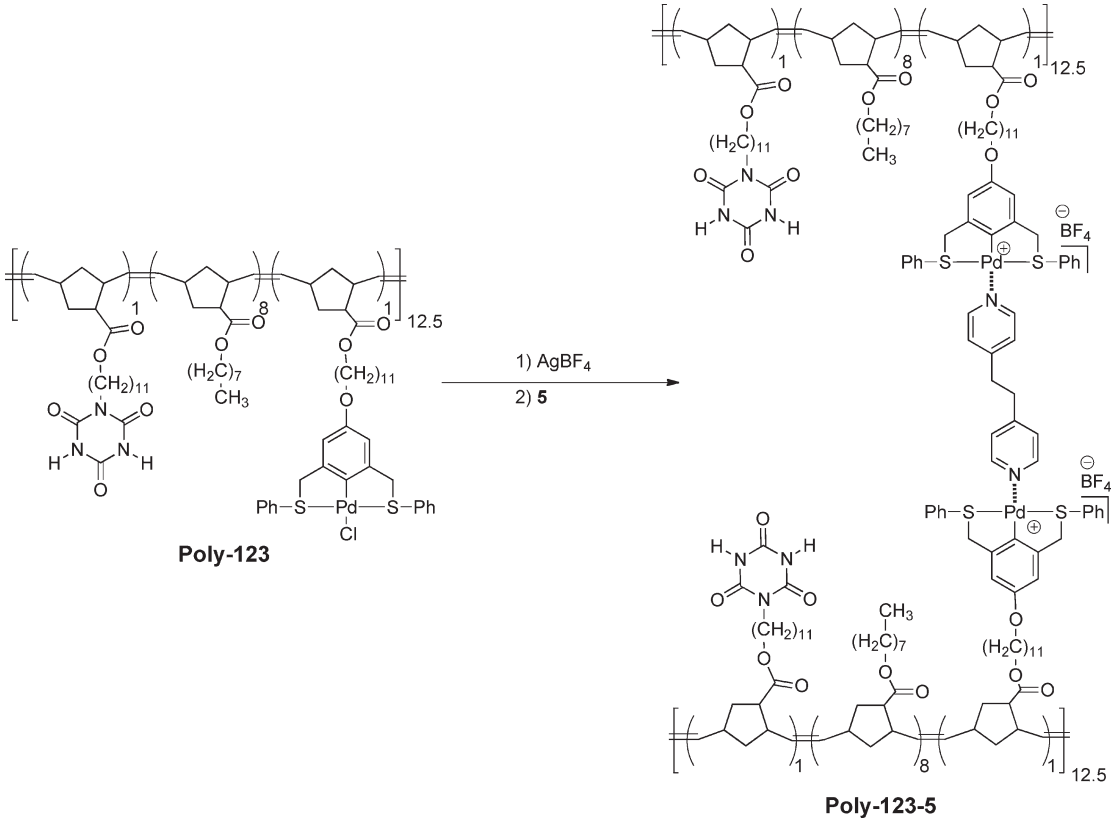
Scheme 3. Schematic Representation of the Noncovalent Cross-Linking of Poly-123 via Metal Coordination Using 5



by rheology as well as visually. Figure 3 shows a plot of G' and G'' versus the amount of **4** for **Poly-123**. Solutions of **Poly-123-4** containing less than 20 mol % of **4** mainly yielded viscous fluids. When the concentration of **4** was increased above 25 mol %, elastic gels were obtained which did not flow under gravity after vial inversion (Figure 4A). These gels were stable for months at room temperature. We suggest that the high cross-linking efficiency of **4** can be explained by the formation of multipoint hydrogen bonding interactions with the cyanuric acid to form a sample-spanning network structure. However, other factors such as $\pi-\pi$ stacking or aggregate formation cannot be excluded from acting as potential contributing factors to the network formation. These results are consistent with our previous findings[44] and also confirm that the presence of the SCS Pd pincer side chains does not interfere in the formation of the hydrogen bonded interchain cross-links.

We next investigated the cross-linking of **Poly-123** using metal coordination between the palladated pincer complexes and **5**. The cross-linking of **Poly-123** via metal coordination occurs in two steps. First, the palladium centers are activated by substituting the chlorine atoms with tetrafluoroborate anions through the addition of $AgBF_4$.[2,31,41,42,49,55] The mechanism of this metal coordination can be hypothesized by the fact that the pyridine coordinates to the activated Pd centers as shown in Scheme 3, resulting in metal coordinated networks **Poly-123-5**. Possible solvent interactions (in our case 1-chloronaphthalene) in this mechanism have not been investigated in detail and cannot be excluded. To ensure material homogeneity, the gels were allowed to anneal at 80 °C for 4−5 h and rested for at least 12 h at room temperature before rheological analysis.

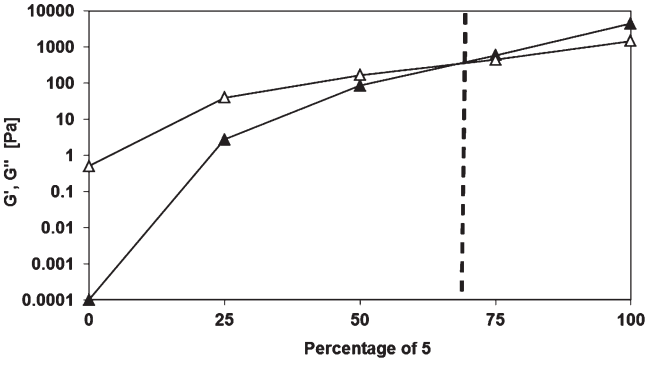
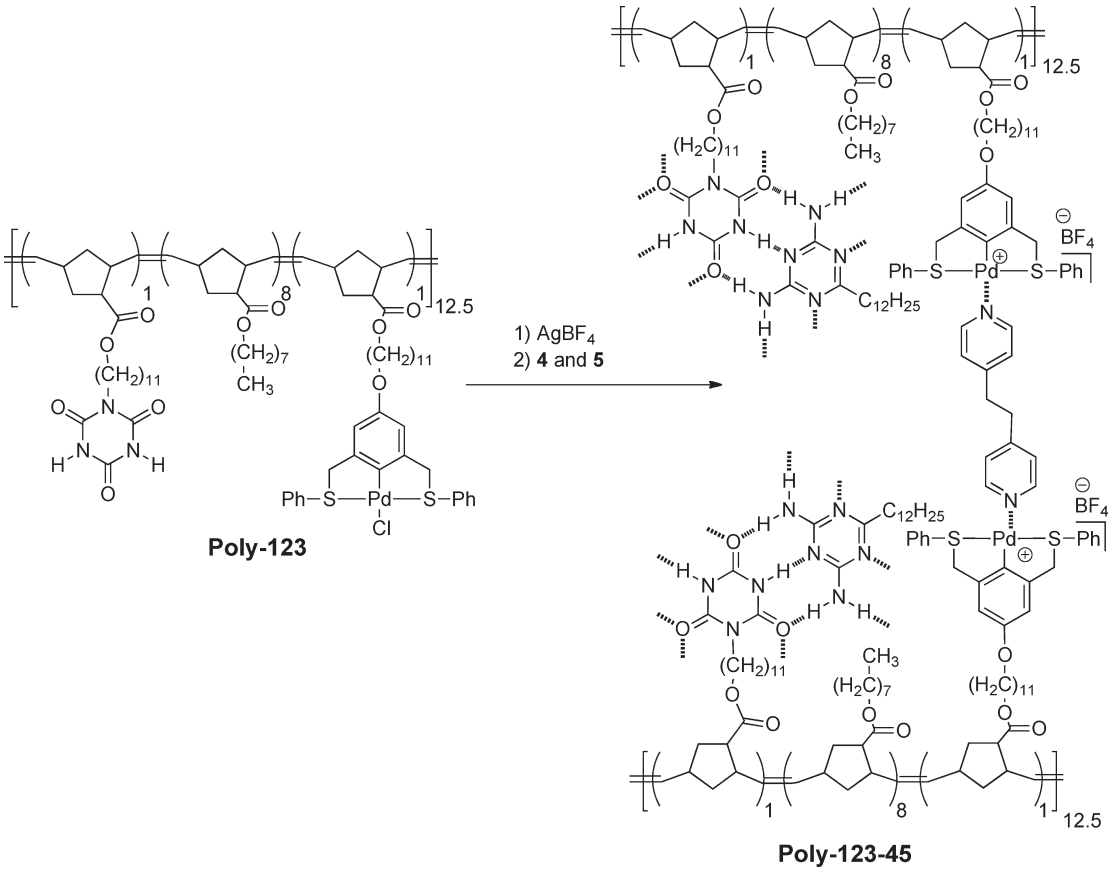


Figure 5. Plot of G' and G'' versus the amount of **5** for **Poly-123**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at a strain value of 0.1 and an angular frequency of 6.28 rad/s. The percentage of **5** is based on the SCS Pd pincer complexes attached to the polymer.

A plot of G' and G'' of **Poly-123** using varying concentrations of **5** (0% to 100% molar ratio of functional groups in the cross-linking agent to pincer groups attached to the polymer chains) is shown in Figure 5. For **Poly-123-5**, the transition from the liquid to the viscoelastic gel state takes place at much higher concentration of **5** (∼75 mol %) in comparison to the previously described hydrogen bonding cross-linking methodology (vial B in Figure 4 illustrates **Poly-123-5** at a 100% cross-linking agent concentration). This result suggests that **4** is a significantly more

Scheme 4. Schematic Representation of the Noncovalent Cross-Linking of Poly-123 via the Addition of 4 and 5



efficient cross-linking agent than **5**. This can be rationalized by the hypothesis that the hydrogen bonded network structure represents a true multipoint array network with high interchain connectivity[44] while the metal cross-linked network consists of strong point-to-point linkages between Pd centers through **5** but has no multipoint array formation.

Multi-Cross-Linking Methodology. The orthogonality of hydrogen bonding between cyanuric acid and 2,4-diaminotriazine as well as metal coordination between pyridine and Pd pincer complexes has been proven by us extensively over the past years.[2,41,42,49,50] Furthermore, metal coordination using palladated pincer complexes occurs at mild conditions and can be combined successfully with hydrogen bonding without causing any deleterious side reactions.[31,41,49,51] These characteristics make the cyanuric acid/2,4-diaminotriazine and SCS Pd pincer complex/pyridine recognition pairs the suitable combination for developing a multifunctional cross-linking strategy based on hydrogen bonding and metal coordination. The multi-cross-linking was carried out in 1-chloronapthalene at room temperature by first adding $AgBF_4$ to **Poly-123** followed by the addition of **4** and **5** to the reaction mixture. The resulting mixtures were annealed at 80 °C for 4 h and rested at room temperature for at least 12 h followed by rheological characterization.

The degree of cross-linking can be controlled by varying the concentration of both of the cross-linking agents (the concentrations of both **4** and **5** were kept equimolar) from 0% to 100% (molar ratio of functional groups in the cross-linking agent to cyanuric acid groups as well as the metalated pincer complexes attached to the polymer chains).

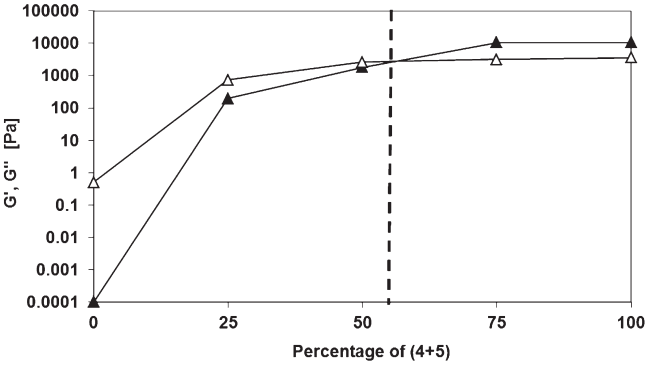


Figure 6. Plot of G' and G'' versus the amount of **4** + **5** [1:1 mole ratio] for **Poly-123**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at a strain value of 0.1 and an angular frequency of 6.28 rad/s. The percentage of **4** is based on the cyanuric acid groups attached to the terpolymer, whereas the percentage of **5** is based on the SCS palladium pincer complex groups attached to the terpolymer.

A plot of G' and G'' versus the amount of **4** + **5** [1:1 mole ratio] for **Poly-123** is depicted in Figure 6. The system undergoes gelation at cross-linking agent concentration of 57%, which falls in between the gelation points of **Poly-123-4** and **Poly-123-5** (vial C in Figure 4 illustrates **Poly-123-45** at a 100% cross-linking

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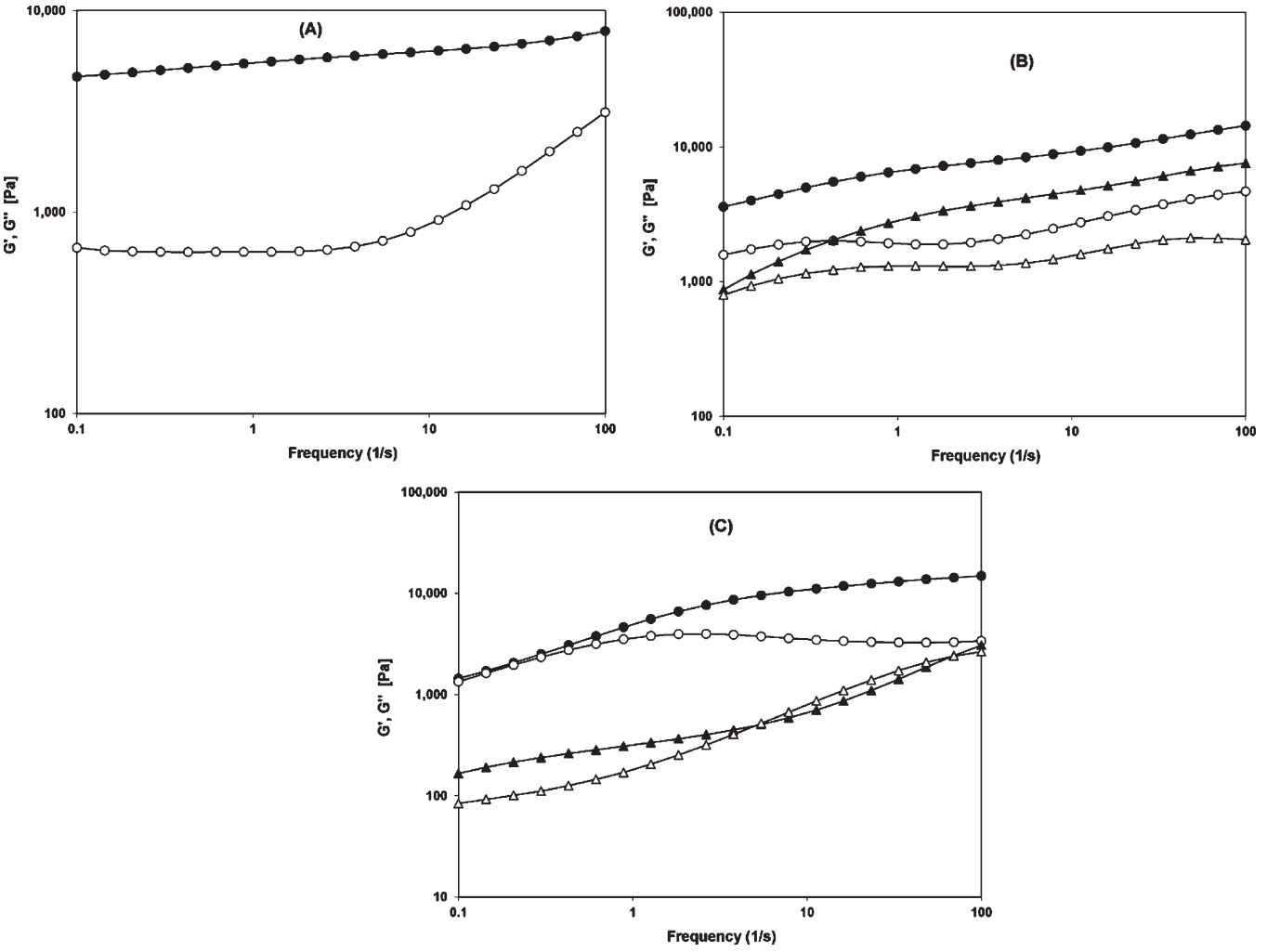

Figure 7. Frequency sweeps at 20 °C (circles) and at 80 °C (triangles) at a strain amplitude of 0.1 for (A) **Poly-123-4** (data at 80 °C was too low to be accurately plotted), (B) **Poly-123-5**, and (C) **Poly-123-45**. Filled symbols denote the elastic modulus [G'], and empty symbols denote the loss modulus [G''].

agent concentration). The cross-linking profile also reveals that the network of **Poly-123-45** is stronger (i.e., higher dynamic modulus) than either **Poly-123-4** or **Poly-123-5** at the corresponding cross-linking agent compositions, indicating that the two interactions do not inhibit each other in the gel forming process. Furthermore, Figure 6 shows that the dynamic modulus reaches a saturation point above 75% cross-linking agent concentration; i.e., further addition of **4** and **5** does not increase the modulus of the network. Clearly, the mechanical properties of these networks can be varied easily by varying the proportions of the cross-linking agents, an important advantage in comparison to self-associative polymer networks.

The role of the solvent in this system is crucial. The multifunctional cross-linking methodology described here will work only in a solvent that is nondisruptive to both cross-linking mechanisms. For example, a polar protic solvent can significantly weaken the hydrogen bonding interactions, resulting in a much weaker hydrogen bonded network. Similarly, in a highly coordinating solvent such as pyridine, the metal coordination interaction with the coordinating solvent will weaken the metal interchain cross-links. We found 1-chloronaphthalene to be a suitable solvent for our studies since it does not cause any observable interference with either the hydrogen bonding or the metal coordination cross-linking. However, a detailed investigation of the effect of 1-chloronaphthalene either on the hydrogen bonding or the metal coordination step has not been carried out.

To probe the effect of both cross-linking agents on the network structure more quantitatively, we carried out oscillatory measurements with a cone-and-plate rheometer with a polymer concentration of 10 wt % in 1-chloronapthalene and 100% cross-linking agent concentration. The viscoelastic behavior of these gels was investigated by performing frequency sweeps at 20 and at 80 °C (Figure 7).

The frequency plot for **Poly-123-4** shows that the hydrogen bonded network exhibits viscoelastic properties with a high G' when measured at 20 °C. The unusual increase in G'' with frequency has been observed before for hydrogen bonded transient networks but needs further investigation into the mechanism of network response.[56] However, the entire network structure falls apart at higher temperatures, and the data obtained at 80 °C were too low to be measured accurately within the error margin of the instrument. The metal coordinated network **Poly-123-5** retains its viscoelastic behavior even at elevated temperatures. The multifunctionalized **Poly-123-45** also retains its

Table 1. Results of the Rheological Characterization of Poly-123, Poly-123-4, Poly-123-5, Poly-123-45, Poly-123-45-6, Poly-123-45-7, and Poly-123-45-67[a]

entry	polymer/network	state	G'/G''	$\lvert G^*\rvert$
Poly-123	un-cross-linked	liquid	<0.01	0.73
Poly-123-4	hydrogen bonded cross-linked	viscoelastic gel	7.77	6250
Poly-123-5	metal coordinated cross-linked	viscoelastic gel	3.05	4690
Poly-123-45	multifunctionalized cross-linked	viscoelastic gel	2.88	110050
Poly-123-45-6	selective hydrogen bond de-cross-linked	viscoelastic gel	1.03	7520
Poly-123-45-7	selective metal coordination de-cross-linked	viscoelastic gel	3.05	4910
Poly-123-45-67	multifunctionalized de-cross-linked	liquid	<0.01	0.24

[a] G'/G'' and $\lvert G^*\rvert$ values measured at an angular frequency of 1 Hz at 20 °C. All values are measured for polymer solutions (10 wt %) in 1-chloronaphthalene. All cross-linking agents and de-cross-linking agents have been added as 100% equivalent to the appropriate recognition units along **Poly-123**.

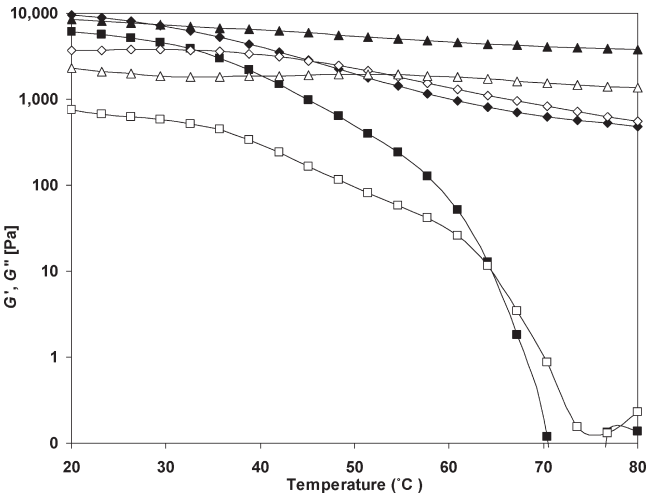

Figure 8. Temperature sweep profiles of **Poly-123-4** (rectangles), **Poly-123-5** (triangles), and **Poly-123-45** (diamonds) from 80 to 20 °C. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G'']. G' and G'' were measured at ω = 6.28 rad/s and a strain of 0.1.

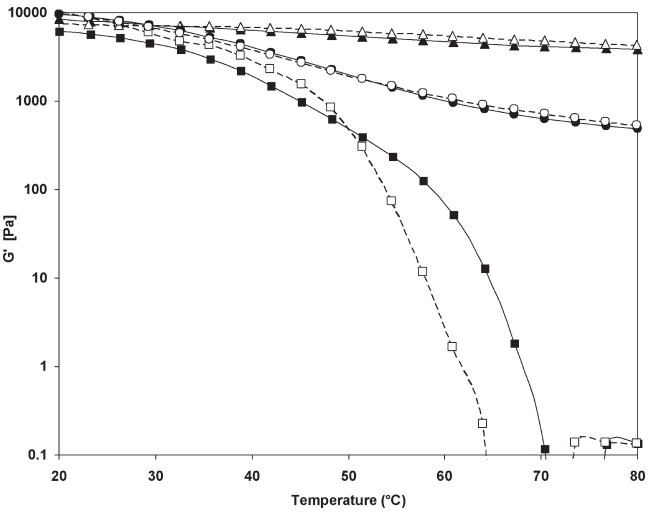

Figure 9. Thermal recovery of G': (1) 20 to 80 °C (heating cycle: filled symbols) and (2) 80 to 20 °C (cooling cycle: empty symbols) for **Poly-123-4** (rectangles), **Poly-123-5** (triangles), and **Poly-123-45** (circles). G' was measured at ω = 6.3 rad/s and a strain of 0.1.

viscoelastic behavior at higher temperatures; however, the loss of moduli is higher than that of the metal coordinated network which can be explained by the loss of the hydrogen bonding based cross-links; i.e., this system allows for switchable cross-linking density by increasing the temperature. The observations from the frequency sweeps for these networks are summarized in Table 1. All networks have $G'/G'' > 1$ and significant $\lvert G^*\rvert$ values confirming their viscoelastic nature.

Figure 8 shows a strong temperature dependence of **Poly-123-4** which essentially becomes a low-viscosity liquid between 60 and 70 °C with $G' < G''$. The decrease in moduli is impressive with a loss of 99.99% at 80 °C (by more than a factor of 40 000) exhibiting a strong thermal response as was shown in our previous work.[44] In contrast, the metal coordination cross-linking in **Poly-123-5** is sufficiently stable such that the network still behaves as a viscoelastic gel even at 80 °C with $G' > G''$. Multifunctional cross-linked network **Poly-123-45** shows an intermediate thermal response, which is significantly less than **Poly-123-5** but stronger than **Poly-123-4** due to the presence of the highly thermally responsive hydrogen bonding interactions along with the relatively low thermally responsive metal coordination interchain cross-links.

In order to probe the thermal reversibility of the polymer networks in more detail, we conducted a temperature sweep in which the sample was subjected to a heating−cooling cycle which consisted of first increasing the temperature from 20 to 80 °C and then lowering it back to 20 °C with heating and cooling rates of 2 °C/min while monitoring the G' and G'' values of the networks. During both the heating and cooling cycle, the viscoelastic moduli were monitored at a constant frequency (6.28 rad/s) and strain amplitude (0.1). One of the important parameters of the study was to determine the recovery of the moduli after the networks have been exposed to higher temperatures. Figure 9 depicts the thermal recovery of G' of these networks; the filled symbols denote the G' values during the heating cycle from 20 to 80 °C, whereas the empty symbols depict the G' values during the cooling cycle from 80 to 20 °C.

It can be seen that **Poly-123-4** shows a large hysteresis with the G' showing about a 70% increase after being subjected to the heating cycle. This phenomenon can be attributed to the fact that **Poly-123-4** being a hydrogen bonded network is highly thermally sensitive and essentially gets completely de-cross-linked at 80 °C, thereby relieving all the stresses in the network. When the system is gradually cooled back to 20 °C,

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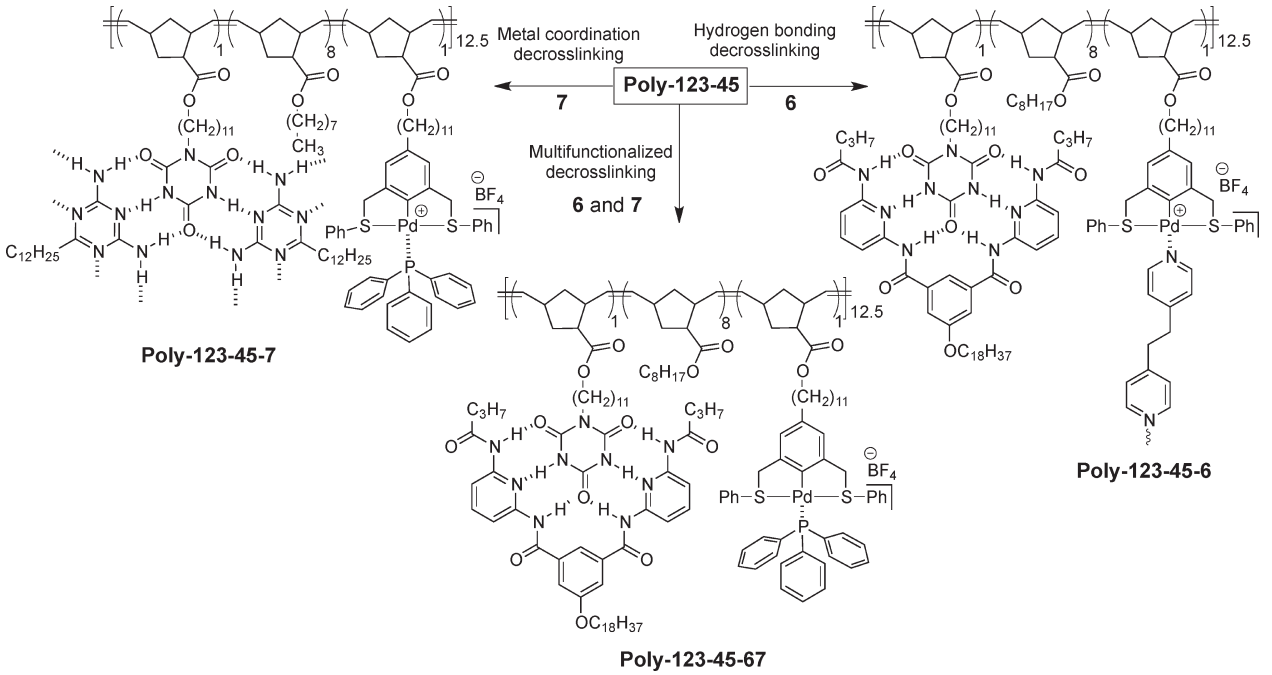
Scheme 5. Multifunctional Noncovalent De-Cross-Linking Strategies for Poly-123-45



the network re-forms stronger with lower stress levels and thus exhibits higher moduli.

The metal network **Poly-123-5** and the multifunctionalized **Poly-123-45**, however, show lower thermal sensitivity and do not undergo complete thermal de-cross-linking, and consequently there is no re-forming of a more stable network during the cooling cycle; hence, they almost quantitatively recover. This experiment also depicts the thermal stability of these networks as they do not lose moduli after the thermal cycle.

De-Cross-Linking Studies. Since the hydrogen bonding and metal coordination processes utilized here have been shown to be orthogonal to each other,[2,41,42,50] we can use this orthogonality for selective as well as for simultaneous de-cross-linking of the fully multi-cross-linked **Poly-123-45**. It has been demonstrated that under identical conditions the three-point hydrogen bonding system between cyanuric acid and 2,4-diaminotriazine has a lower association constant than the six-point hydrogen bonding system between cyanuric acid and the Hamilton wedge (Figure 1A-2).[44,45,52] Such a difference in the stability of these complexes can be exploited to selectively disrupt the weaker hydrogen bonded complex in the favor of the stronger one. This displacement process can be utilized to de-cross-link the hydrogen bonded interchain cross-links selectively. Hence, the addition of monotopic **6** to **Poly-123-45** should result in the disruption of the three-point hydrogen bonded complex between cyanuric acid and **4**, thus breaking the hydrogen bonded interchain cross-links between the polymer chains leading to partly side-chain-functionalized metal coordinated network **Poly-123-45-6** as shown in Scheme 5. Because of the orthogonal nature of the hydrogen bonding and metal coordination interactions, the addition of **6** is not expected to disrupt the metal coordinated interchain linkages, and thus **Poly-123-45-6** is expected to behave as a metal cross-linked material with low-temperature responsiveness as compared to **Poly-123-5**.

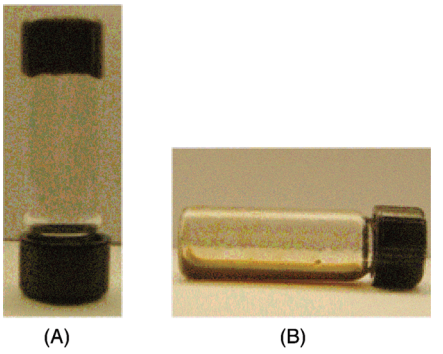


Figure 10. Inverted vials with (A) **Poly-123-45** (viscoelastic gel) and (B) **Poly-123-45-67** (free-flowing liquid) at room temperature. The polymers and additives were dissolved in 1-chloronaphthalene.

Palladated SCS pincer−pyridine complexes have been known to be disrupted by the addition of triphenylphosphine which acts as a ligand displacement agent;[53−55] hence, the addition of **7** to **Poly-123-45** should result in the selective de-cross-linking of the Pd−pyridine interchain cross-links by the formation of the stronger side-chain-functionalized SCS Pd−triphenylphosphine complexes to form **Poly-123-45-7**, as shown in Scheme 5. **Poly-123-45-7** should still be cross-linked via interchain hydrogen bonding between the pendant cyanuric acid and **4**; thus, the network should behave as a completely hydrogen bonded cross-linked system (similar to **Poly-123-4**) and should show high thermal responsiveness.

Finally, **Poly-123-45** can be de-cross-linked completely via a multiple-cross-linking strategy. The addition of both **6** and **7** to **Poly-123-45** should result in de-cross-linking of both the metal coordination as well as hydrogen bonded interchain cross-links, respectively, and should result in completely de-cross-linked and side-chain-functionalized polymer **Poly-123-45-67** in which the

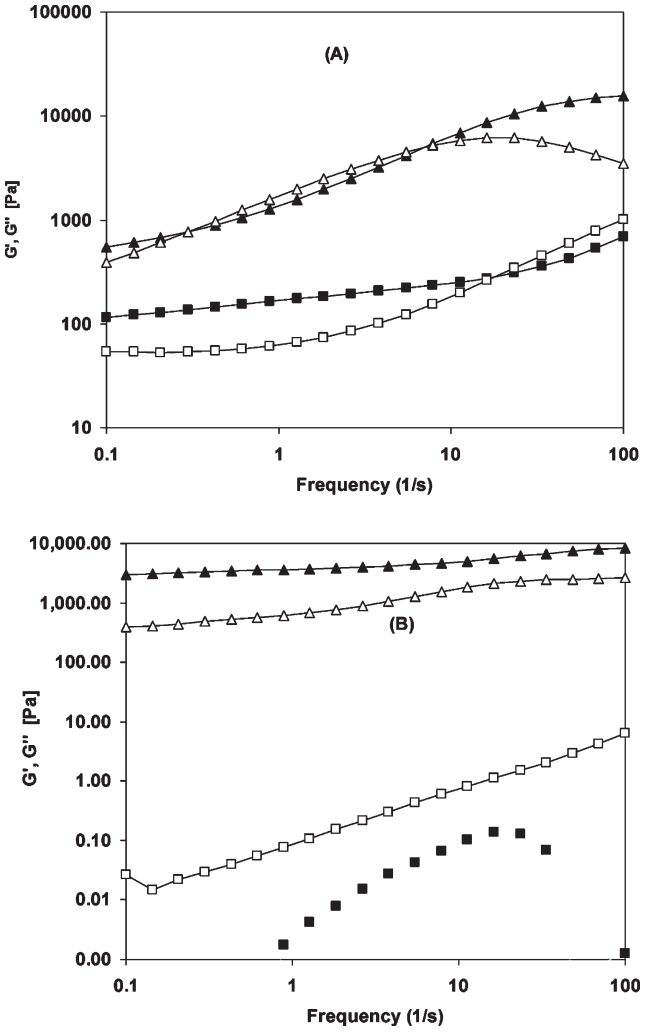


Figure 11. Frequency sweeps at 20 °C (triangles) and at 80 °C (squares) at a strain amplitude of 0.1: (A) **Poly-123-45-6** and (B) **Poly-123-45-7**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G'']. Plots of **Poly-123-45-67** have not been included due to their very low moduli values.

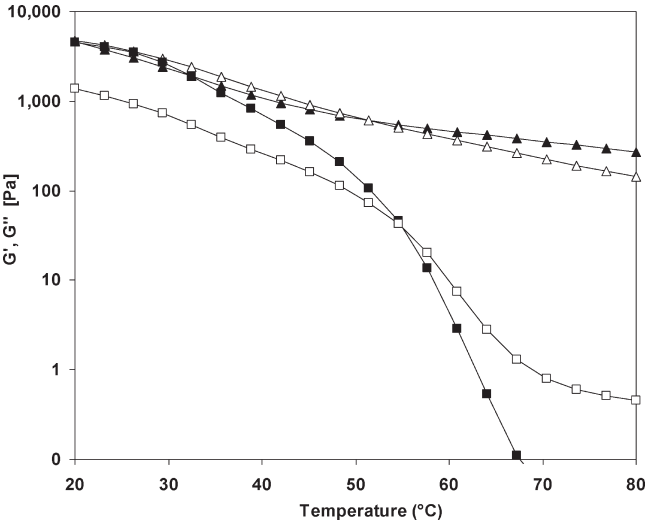


Figure 12. Temperature sweep profiles from 20 to 80 °C for **Poly-123-45-6** (triangles) and **Poly-123-45-7** (squares). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G'']. Data were measured at ω = 6.3 rad/s and a strain of 0.1.

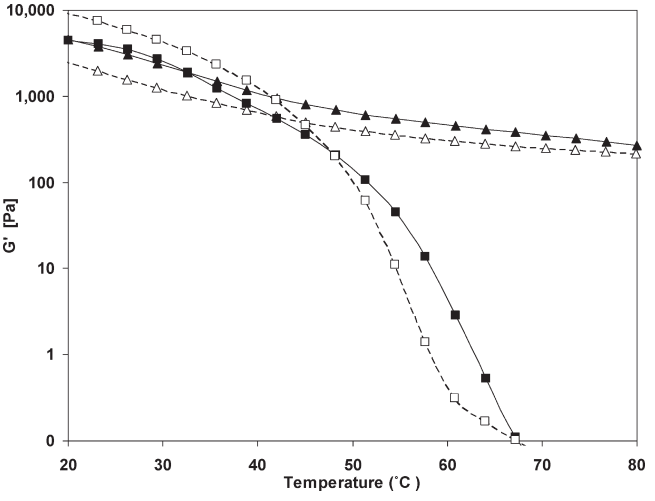


Figure 13. Thermal reversibility: Temperature sweeps of G': 20 to 80 °C (heating cycle: filled symbols) and 80 to 20 °C (cooling cycle: empty symbols) for **Poly-123-45-7** (rectangles) and **Poly-123-45-6** (triangles). G' was measured at ω = 6.3 rad/s and a strain of 0.1.

cyanuric acid groups are end-capped with monotopic **6**, whereas the palladated SCS pincer complexes are end-capped with **7** (Scheme 5). Hence, by using this multifunctional de-cross-linking strategy, a viscoelastic gel of **Poly-123-45** should be completely de-cross-linked to form a free-flowing liquid. We initially investigated these de-cross-linking hypothesis using vial inversion tests. As shown in Figure 10, upon the addition of one equivalent of each of the de-cross-linking agents **6** and **7**, **Poly-123-45** was transformed from a highly viscoelastic gel to a free-flowing liquid **Poly-123-45-67**.

After the preliminary de-cross-linking studies, we investigated the selective and multi-de-cross-linking strategies via rheology. Figures 11 and 12 show the frequency and temperature sweep profiles of **Poly-123-45-6** and **Poly-123-45-7**, respectively. **Poly-123-45-6** shows viscoelastic behavior very similar to **Poly-123-5**, which we attribute to the fact that both networks have the metal interchain cross-links which are temperature insensitive. Although **Poly-123-45-7** shows $G'' < G'$ at lower temperatures, it undergoes complete de-cross-linking at 80 °C and thus is similar to the purely hydrogen bonded cross-linked **Poly-123-4**. However, it is noteworthy that both **Poly-123-45-6** and **Poly-123-45-7** show almost a 50% increase in the G'' values (and 20% decrease in G') as compared to **Poly-123-5** and **Poly-123-4**, respectively. We do not know the reason for the increase in loss modulii but hypothesize that it could be attributed to the presence of side-chain-functionalized segments in the networks along with the interchain cross-links.

From Table 1, we can see that **Poly-123-45-67**, the fully de-cross-linked material, has a very low G'/G'' (<0.1) as well as $|G^*|$ (0.24), which is similar to the free-flowing un-cross-linked **Poly-123** (Table 1). Hence, the addition of 1 equivalent each of **6** and **7** to **Poly-123-45** results in complete de-cross-linking.

We next investigated the temperature dependence of the selectively de-cross-linked networks. Figure 12 shows a strong temperature dependence of **Poly-123-45-7**, which essentially

becomes a low-viscosity liquid around 60−70 °C with $G' < G''$. This result is very similar to the temperature response of **Poly-123-4** (Figure 8) and strongly indicates that the addition of **7** completely de-cross-links the metal coordination interchain cross-links.

The addition of **6** to **Poly-123-45** should result in selective de-cross-linking of the hydrogen bonded cross-links without significantly affecting the metal cross-links. The data in Figure 12 show that **Poly-123-45-6** is sufficiently stable and behaves as a viscoelastic gel even at 80 °C with $G' > G''$, which is similar to the temperature response of **Poly-123-5** (Figure 8).

We also studied the thermal reversibility of these polymer networks by subjecting them to a heating cycle from 20 to 80 °C and then cooling them from 80 to 20 °C, while monitoring their moduli. Figure 13 depicts the thermal recovery of G' of these networks. **Poly-123-45-7** shows a large hysteresis with almost 100% increase in the G' recovery. This behavior is similar to the purely hydrogen bonded **Poly-123-4**; hence, **Poly-123-45-7** completely de-cross-links thermally which relieves the built-in networks stresses. When the system is cooled down to 20 °C, the network re-forms stronger with a lower degree of stress. However, the metal coordination based network **Poly-123-45-6** like the pure metal cross-linked **Poly-123-5** does not show any increase in the moduli after the thermal cycle.

These data show that **Poly-123-4** and **Poly-123-45-7** show similar thermal behaviors exhibiting large thermal responsiveness as well as positive thermal hysteresis. In contrast, the metal coordinated networks (**Poly-123-5** and **Poly-123-45-6**) show decreased thermal responsiveness. This also suggests that our de-cross-linking strategy allows for the conversion of **Poly-123-45** to a highly thermally sensitive network (**Poly-123-45-7**) or to a chemoresponsive material (**Poly-123-45-6**).

SUMMARY

We have synthesized a multifunctionalized polymer scaffold containing hydrogen bonding and metal coordination molecular recognition motifs in its side chains. This scaffold has been cross-linked reversibly by the addition of small molecule cross-linking agents via either single selective or simultaneous multiple non-covalent molecular recognition strategies to give reversible cross-linked polymer networks. The hydrogen bonded networks produced stable gels via multipoint hydrogen bonding based interchain cross-linking with a high thermal response. In contrast, the metal coordination based cross-linked materials are thermally stable and retained their viscoelastic nature even at elevated temperatures. The orthogonality of these two interactions allowed for multifunctionalized cross-linking by using the two interactions simultaneously in a nondisruptive solvent such as 1-chloronaphthalene. These multifunctionalized cross-linked networks showed intermediate thermal response as compared to the hydrogen and metal cross-linked networks.

The multifunctionalized networks have also been selectively as well as simultaneously de-cross-linked. Whereas the strong metal coordinated polymer networks exhibited chemoresponsiveness and could be completely de-cross-linked using a ligand displacement agent such as triphenylphosphine, the hydrogen-bonded network can be de-cross-linked either physically via temperature or chemically via the addition of a monotopic end-capping agent that forms significantly stronger hydrogen bonds than the cross-linking agent. Since both interactions are fully orthogonal, we de-cross-linked the multifunctionalized polymer network using both interactions to obtain a completely de-cross-linked fully functionalized free-flowing polymer similar to the un-cross-linked terpolymer. Therefore, through the selective addition of cross-linking or de-cross-linking agents to the multifunctionalized polymer we have been able to control and tune the mechanical properties of the resulting networks. By the use of orthogonal multiple noncovalent interactions, we have converted a single polymer backbone which was essentially a free-flowing nonresponsive liquid ($G'/G'' = 0.01$, $|G^*| = 0.7$) to a highly viscoelastic network ($G'/G'' = 2.8-7.7$, $|G^*| = 4700-110\,000$) with responsiveness to either temperature or ligand displacement agents.

This study showcases the unique advantages of simultaneously using orthogonal multiple noncovalent interactions to convert a single polymer backbone to a family of multiresponsive materials. Such a strategy should allow for the generation of a diverse set of materials with different properties being generated from the same parent material.

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