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Complementary Hydrogen-Bonded Thermoreversible Polymer Networks with Tunable Properties

Kamlesh P. Nair,[†] Victor Breedveld,*[,‡] and Marcus Weck*[,†,§]

School of Chemistry and Biochemistry and School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, and Department of Chemistry and Molecular Design Institute, New York University, New York, New York 10003

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ABSTRACT: Complementary hydrogen bonded cross-linked polymer networks based on two distinct hydrogen bonding recognition motifs have been synthesized by using a combination of ring-opening metathesis polymerization and hydrogen bonding interactions and were subsequently characterized in solution using rheometry. The hydrogen bonding recognition units were based on either three-point cyanuric acid−2,4-diaminotriazine or six-point cyanuric acid−Hamilton wedge interactions. Through the addition of "ditopic cross-linking agents", the polymer scaffold, which was functionalized with cyanuric acid functional groups, was noncovalently cross-linked in solution through complementary interchain hydrogen bonding interactions. The extent of cross-linking could be controlled by varying the amount of the cross-linking agent added. These networks are thermally reversible and have highly tunable mechanical properties that are controlled by the molecular structure of the cross-linking agent. While the addition of the Hamilton wedge cross-linking agent to the polymer solution led to high-viscosity fluids, the 2,4-diaminotriazine cross-linking agent produced highly viscoelastic gels. It is hypothesized that this is due to a higher degree of connectivity between the cross-linking agent and the polymer in spite of the inherently weaker hydrogen bonding (three- vs six-point). The study shows that the microstructure plays an important role in the macroscopic mechanical properties of these hydrogen bonded networks in solution. By varying the hydrogen bonding motif, materials with tunable rheological properties were obtained from the same parent polymer backbone. Such a strategy will allow for materials design by tailoring the network microstructure via the molecular architecture of the cross-linking agents.

Introduction

Cross-linked polymer networks have superior mechanical properties and increased thermal and chemical resistance in comparison to their un-cross-linked and linear analogues.[1–6] Traditionally, covalent approaches have been used for the cross-linking step. Although highly successful, these strategies result in irreversible polymer networks with severe limitations such as a lack of control over the final network architecture, potential side reactions (e.g., chain degradation), and limited processability.[7] In response to these shortcomings, scientists have explored the employment of reversible and bidirectional reactions for cross-linking, including reversible Diels−Alder adducts,[8,9] mechanically interlocked systems such as rotaxanes,[10] photochemically reversible systems such as coumarins,[11,12] and polymer systems with tunable morphological variations.[13] These reversible and bidirectional processes allow for cross-linking without extensive chain degradation and often proceed without side reactions, thus providing a greater degree of control over the final network architecture. A second successful strategy to overcome the limitations of covalent cross-linking is the use of noncovalent interactions as key interchain interactions for reversible cross-linking, for example, hydrogen bonding,[14,15] metal coordination,[16–18] Coulombic interactions,[19,20] and dipole−dipole interactions.[21,22] One important advantage of noncovalent cross-linking is its inherently reversible nature that allows for the responsiveness of the final cross-linked network toward a variety of external stimuli including temperature, solvent composition, and pH.[23] Ionomers are one commercially successful example of this strategy that utilizes Coulombic interactions for noncovalent cross-linking.[20,24] Other examples include the use of metal coordination to create materials that are responsive to redox reactions and metal−ligand displacement agents[25,26] and hydrogen bonding to create cross-linked polymer networks that are sensitive to temperature. In this contribution, we report a highly tunable, thermally reversible polymeric network based on complementary hydrogen bonding. We demonstrate that one can fine-tune network properties in solution by choosing the appropriate hydrogen bonding interaction, while the extent of cross-linking can simultaneously be tuned via the concentration of the cross-linking agent added. As a result, these materials offer a high degree of control over the final mechanical properties, and the underlying strategy shall be useful in designing tailor-made materials.

Hydrogen bonding is among the most widely used noncovalent interactions for the synthesis of reversible cross-linked polymeric networks.[14,15] It has been employed extensively in polymer blends where hydrogen bonding between functional groups attached to often immiscible polymers results in a miscible blend consisting of the network of two distinct polymers.[27] Hydrogen bonds are thermally reversible and the strength of hydrogen bonded complexes can be tuned easily by (i) varying the number of hydrogen bonds from single,[28] dual,[29,30] triple,[26] quadruple[27] to sextuple or even higher order hydrogen bonding motifs,[31,32] (ii) changing solvent or temperature,[33] or (iii) altering the acidity and/or basicity of the donor (D) and acceptor (A) moieties.[34] In polymer melts, even weak hydrogen bonded complexes can be used for polymer cross-linking when combined with additional stabilization factors. Rowan and co-workers have used telechelic polymers based on adenines and cytosines which form weakly bonded hydrogen bonded complexes (association constant $<5\ M^{-1}$). They found that the combination of weak hydrogen bonding with phase separation resulted in thermally sensitive cross-linked polymer melts.[35]

* Corresponding authors. E-mail: victor.breedveld@chbe.gatech.edu or marcus.weck@nyu.edu.
[†] School of Chemistry and Biochemistry, Georgia Institute of Technology.
[‡] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology.
[§] New York University.

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Polymeric networks based on hydrogen bonding can be classified broadly into two classes distinguished by the origin of cross-links due to (a) self-association or (b) addition of an external "cross-linking agent". In self-associative polymeric networks, often referred to as one-component systems, the hydrogen bonding recognition units are attached covalently to the polymer backbone and exhibit a strong tendency for self-association, i.e., dimerization, which results in interchain cross-linking. Such systems are inherently cross-linked and do not require external cross-linking agents. Examples include the systems developed by Stadler and co-workers, who extensively studied reversible polymer network formation via intermolecular hydrogen bonding of urazoylbenzoic acid-functionalized poly(isobutylene),[29,30] and by Coates and co-workers, who synthesized reversible thermoplastic elastomers based on self-dimerizing ureidopyrimidone units.[36] While the strategy of using self-associative interactions for interchain cross-linking is highly successful in controlling the network structure, an important limitation is that these systems are always "cross-linked" and would exhibit "un-cross-linked" behavior only at temperatures above the hydrogen bond dissociation temperature. Furthermore, these systems lack the flexibility to change the strength and degree of cross-linking: synthesis of new polymeric systems is typically required to modify the network properties.

The second category of hydrogen bonded polymeric networks utilizes complementary hydrogen bonding interactions with small molecule "cross-linking agents" to achieve cross-linking. In these two-component systems, the hydrogen bonding recognition units attached to the polymer backbone undergo little or no self-association and cannot effectively "cross-link" the polymer chains; instead, an external "cross-linking agent" has to be added. The cross-linking agent undergoes directed hydrogen bonding with multiple recognition motifs along polymer chains to cross-link them through interchain hydrogen bonding. In such a system, the degree of cross-linking can be tuned from "un-cross-linked" to fully "cross-linked" by varying the amount of cross-linking agent. Moreover, subtle changes in the chemistry of the cross-linking agent can be used to further modify the network structure. Kato and co-workers have used this approach to cross-link supramolecular side-chain liquid crystalline polymers by using bis-pyridine as the cross-linking agent.[37] They thus achieved an increase of mesophase stability of the liquid crystalline state.[37] Rotello and co-workers employed bis-thymine-based cross-linking agents with different linker lengths to reversibly cross-link 2,6-diaminopyridine-functionalized copolymers and form discrete micron-sized spherical polymeric aggregates.[33] They demonstrated that the linker length influences the median diameter of the spherical aggregates and that the aggregate dimensions can be controlled further by varying the molecular architecture of the cross-linking agent. In a recent contribution, we have demonstrated that it is possible to tune the strength of cross-linking and the solution viscosity by choosing the appropriate complementary hydrogen bonding recognition units.[26] These examples illustrate the importance of the molecular architecture of the cross-linking agent in determining the network structure. In this study, we extend this approach by using a recognition motif attached to the polymer backbone that is able to form different hydrogen bonding motifs with cross-linking agents. Our hypothesis is that such a system will allow us to tailor the materials properties in solution, in particular the degree of cross-linking and strength of the network. Such networks based on multiple hydrogen bonding interactions have the potential to be used in the fabrication of highly functionalized "smart materials" with tunable thermal responsiveness.

Experimental Section

General. All reagents were purchased either from Acros Organics, Aldrich, or Strem Chemicals and used without further purification unless otherwise noted. Triethylamine (NEt_3), tetrahydrofuran (THF), methylene chloride, and deuterated chloroform ($CDCl_3$) were distilled over calcium hydride. Grubbs' first generation initiator was purified by filtration using purified benzene under an atmosphere of argon. The cyanuric acid monomer (**2**),[38] spacer monomer (**1**),[26] *N*-(6-aminopyridin-2-yl) butyramide,[32] 5,5′-(decane-1,10-diylbis(oxy))diisophthalic acid,[39] 1,4-bis (10-bromodecyloxy)benzene,[40] 6-dodecyl-1,3,5-triazine-2,4-diamine (monotopic 2,4-diaminotriazine),[41] and N^1,N^{10}-bis(6-aminopyridin-2-yl)decanediamide (**7**)[42] were synthesized according to published procedures. 1-Chloronaphthalene, dicyandiamide, and 5-octyldecyloxyisophthalic acid were used as received. ^{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). High-resolution mass spectra (HTMR) were provided by the Georgia Tech Mass Spectrometry Facility on a VG-70se spectrometer using fast atom bombardment ionization method (FAB), electron ionization (EI), or MALDI techniques. 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 of American 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 using 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 of polymer solutions at elevated temperature in a cone−plate geometry (diameter 50 mm, angle 1°).[43] All measurements were carried out in oscillatory mode in order to probe the equilibrium structures of the polymer solutions.

11,11′-(1,4-Phenylenebis(oxy))diundecanenitrile. 1,4-Bis(10-bromodecyloxy)benzene (2.19 g, 0.0039 mol) and NaCN (0.78 g, 0.0156 mol) were suspended in DMSO (100 mL) and heated at 80 °C for 4 h. The solvent was removed by distillation under reduced pressure. Then, CH_2Cl_2 (200 mL) was added. The resulting solution was extracted with water (3 × 100 mL), and the organic phase was dried using anhydrous magnesium sulfate. The solvent was removed to give the product as a white solid (1.5 g, 85%). ^{1}H NMR ($CDCl_3$): δ = 6.71 (s, 4H, Ar), 3.79 (t, 4H, J = 6.38 Hz, $-OCH_2-$), 2.29 (t, 4H, J = 7.08 Hz, $-CH_2-CN$), 1.64 (p, 4H, J = 6.64 Hz, $-OCH_2-CH_2-$), 1.56 (m, 4H, $-CH_2-CH_2-CN$), 1.32−1.21 (m, 24H, $-(CH_2)_4-$). ^{13}C NMR ($CDCl_3$): δ = 153.3, 120.1, 115.5, 68.7, 41.2, 29.6, 29.5, 29.4, 28.9, 28.8, 26.2, 25.5, 17.3. HRMS (FAB+) [M + 1] calcd for $C_{28}H_{44}N_2O_2$: 441.34810, found: 441.34744.

6,6′-(10,10′-(1,4-Phenylenebis(oxy))bis(decane-10,1-diyl))bis-(1,3,5-triazine-2,4-diamine) (3). 11,11′-(1,4-Phenylenebis(oxy))-diundecanenitrile (1.38 g, 0.0031 mol), dicyandiamide (0.75 g, 0.0124 mol), and KOH (1.00 g) were dissolved in 1-propanol (100 mL), and the reaction mixture was refluxed for 12 h. The solvent was removed by distillation under reduced pressure, and the residue was washed with hot water (100 mL) and dried. Repeated recrystallization out of ethanol yielded the final product as a pale yellow solid (3.40 g, 45%). ^{1}H NMR (DMSO-d_6): δ = 6.79 (s, 4H, Ar), 6.65 (8H, br s, $-NH_2$), 3.84 (t, 4H, J = 6.38 Hz, $-CH_2O-$), 2.29 (p, 4H, J = 6.60 Hz, $-CH_2CH_2O-$), 2.02 (t, 4H, J = 7.1 Hz, $-CH_2-$), 1.64−1.03 (m, 28H, $-(CH_2)_7-$). ^{13}C NMR (DMSO-d_6): δ = 178.4, 167.7, 153.2, 115.9, 68.4, 38.6, 29.6, 29.5, 29.4, 28.8, 27.8, 26.2, 25.3, 16.7. HRMS (FAB+) [M + 1] calcd for $C_{32}H_{52}N_{10}O_2$: 609.43530, found: 609.43197.

5,5′-(Decane-1,10-diylbis(oxy))bis(N^1,N^3-bis(6-butyramidopyridin-2-yl)isophthalamide) (4). 5,5′-(Decane-1,10-diylbis(oxy))diisophthalic acid (1.00 g, 1.99 mmol) was dissolved in thionyl chloride (5 mL). A few drops of anhydrous DMF were added, and the reaction mixture was heated at 80 °C for 12 h after which the excess thionyl chloride was distilled off. The crude acid chloride was washed with anhydrous THF to remove excess thionyl chloride and dried under high vacuum at room temperature. The acid chloride was then cannula transferred into a solution of *N*-(6-aminopyridin-2-yl)butyramide (2.13 g, 11.9 mol) and NEt_3 (40 mL) in anhydrous THF (100 mL) at 0 °C. The solution was allowed to stir at room temperature for 12 h, after which it was filtered to remove any insoluble products. The solvent was evaporated, and the residue was repeatedly washed with water to remove all triethylamine salts and finally dried. The residue was suspended in ethyl acetate and stirred for 30 min and then filtered to recover the product. To ensure complete removal of the unreacted amine, the product was repeatedly washed with ethyl acetate to give the product as a gray powder (1.03 g, 45%). ^{1}H NMR (DMSO-d_6): δ =10.45 (s, 4H, −CONH−), 10.08 (s, 4H, −CONH−), 8.07 (s, 2H, Ar), 7.80−7.72 (m, 12 H, pyridyl), 7.66 (s, 4H, Ar), 4.11 (t, 4H, J = 6.50 Hz, $-CH_2O-$), 2.35 (t, 8H, J = 7.1 Hz, $-CONH-CH_2-$), 1.74 (m, 4H), 1.60 (m, 8H, $-CONH-CH_2-CH_2-$), 1.41−1.31 (m, 12H), 0.85 (t, 12H, J = 7.2 Hz, $-CH_3$). ^{13}C NMR (DMSO-d_6): δ = 171.5, 164.4, 158.2, 150.1, 149.5, 139.5, 135.1, 115.7, 110.1, 105.6, 67.8, 37.8, 28.8, 28.5, 28.4, 25.3, 18.3. MALDI calcd for: $C_{62}H_{74}N_{12}O_{10}$: 1146.56508, found: 1146.5604.

N^1,N^3-Bis(6-butyramidopyridin-2-yl)-5-(octadecyloxy)isophthalamide (6). 5-Octyldecyloxyisophthalic acid (2.5 g, 0.005 mol) was dissolved in thionyl chloride (5 mL), and a few drops of anhydrous DMF were added. The reaction mixture was heated at 80 °C for 4 h, after which the excess thionyl chloride was distilled off. The crude acid chloride was washed with anhydrous THF and dried under high vacuum at room temperature. The acid chloride was then cannula transferred into a solution of *N*-(6-aminopyridin-2-yl)butyramide (3.00 g, 0.016 mol) and NEt_3 (20 mL) in anhydrous THF (100 mL) at 0 °C. The solution was stirred at room temperature for 12 h and filtered to remove any insoluble products, and the solvent was removed under reduced pressure. The residue was redissolved in chloroform (200 mL) and washed with a 2 M NaOH solution (100 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography using silica and ethyl acetate and hexanes (1/1, v/v) as the eluents to yield the final product as a white waxy solid (2.32 g, 52%). ^{1}H NMR ($CDCl_3$): δ = 10.45 (s, 2H, −CONH−), 10.09 (s, 2H, −CONH−), 8.10 (s, 1H, Ar), 7.82−7.73 (m, 6 H, pyridyl), 7.68 (s, 2H, Ar), 4.10 (t, 2H, J = 6.38 Hz, $-CH_2O-$), 2.36 (t, 4H, J = 7.1 Hz, $-CONHCH_2$), 1.74 (m, 2H), 1.62 (m, 4H), 1.34−1.11 (m, 30 H), 0.91 (t, 6H, J = 7.2 Hz, $-CH_3$), 0.84 (t, 3H, J = 6.8 Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 178.5, 172.1, 164.8, 160.2, 149.9, 149.5, 141.5, 135.9, 117.7, 117.4, 110.4, 110.1, 68.9, 39.7, 36.2, 32.1,29.9, 29.8, 29.6, 29.3, 26.2, 22.9, 18.9, 18.5, 14.3, 13.9, 13.8. HRMS (EI) calcd for: $C_{44}H_{64}N_6O_5$: 756.49382, found: 756.49886.

Polymerizations. The synthesis of the copolymer **Poly-12** is described as a representative example: Monomers **1** (2.70 g, 10.79 mmol) and **2** (503 mg, 1.198 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 78.90 mg ([M]/[I] = 125:1) of the initiator was added to the monomer solution. The solution was stirred at room temperature. 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 solvent. The ^{1}H and ^{13}C NMR spectra of all copolymers are analogous to the ones reported in the literature.[26]

Cross-Linking Experiments. For all cross-linking experiments, the copolymers were dissolved in a calculated amount of 1-chloronaphthalene, and the mixture was stirred overnight at room temperature to ensure a homogeneous solution. Then, a calculated amount of the cross-linking agent was added, and the mixture was stirred briefly at elevated temperature until a homogeneous solution was obtained. The sample was then allowed to rest at room temperature for 12 h before the rheological experiments were carried out.

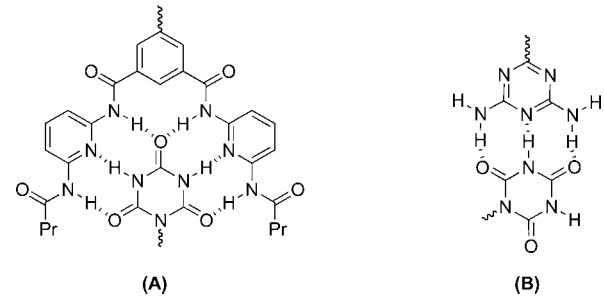


Figure 1. Self-assembly recognition pairs employed in this study: (A) six-point hydrogen bonded complex between the Hamilton wedge receptor and cyanuric acid; (B) three-point hydrogen bonded complex between 2,4-diaminotriazine and cyanuric acid.

The preparation of **Poly-12−3** is described as a representative example: **Poly-12** (200 mg, 0.074 mmol based on the hydrogen bonding functional groups along the polymer backbone) was dissolved in 1.8 g of 1-chloronaphthalene (10 wt %). Then 22.76 mg (0.074 mmol based on the hydrogen bonding sites allowing for quantitative cross-linking) of **3** was added to the sample, and the suspension was heated until a clear homogeneous solution was obtained that quickly gelled when cooled to room temperature. The gel was then allowed to rest at room temperature for least 12 h before rheological measurements were carried out.

Rheological Characterization. The rheological testing protocol of all polymer solutions consisted of (1) strain amplitude sweep at constant frequency (temperature 20 °C; strain amplitude γ = 0.001−10, angular frequency ω = 6.28 rad/s) to identify the linear viscoelastic regime, (2) frequency sweep at constant strain amplitude (20 °C; γ = 0.01; ω = 0.1−100 rad/s) to determine network viscoelasticity, (3) temperature sweep (20 to 80 °C; γ = 0.1; ω = 6.28 rad/s) to characterize thermal stability, (4) frequency sweep at elevated temperature (80 °C; γ = 0.1; ω = 0.1−100 rad/s), (5) temperature sweep (80 to 20 °C; γ = 0.01; ω = 6.28 rad/s) to investigate thermal reversibility, and (6) frequency sweep at constant strain amplitude (20 °C; γ = 0.1; ω = 0.1−100 rad/s) to determine the extent of thermal recovery.

Research Design. Our research design is centered around two different hydrogen bonding interactions utilizing the cyanuric acid recognition motif, which is capable of multiple hydrogen bond formation in two distinct ways: (i) three-point hydrogen bonding between cyanuric acid and 2,4-diaminotriazine and (ii) six-point hydrogen bonding between cyanuric acid and the Hamilton wedge receptor (Figure 1). The six-point hydrogen bonded complex between substituted cyanuric acid residues and the Hamilton wedge receptor has been utilized extensively in supramolecular science because of its high association constant that has been reported to be $\sim 10^6$ M^{-1} in chloroform.[26,32,38,44,45] We have employed this interaction before in side-chain supramolecular polymers.[26,38] In contrast, the three-point hydrogen bonding interaction between cyanuric acid and 2,4-diaminotriazine has not been reported in the literature. However, the interaction between functionalized 2,4-diaminotriazines and functionalized thymines has been reported extensively, giving some precedent to our three-point hydrogen bonding system.[46–49]

We anchor the cyanuric acid moieties covalently onto a poly(norbornene) backbone by copolymerizing monomer **1** and the cyanuric acid containing monomer **2** using ring-opening metathesis polymerization (ROMP). The nonfunctionalized monomer **1** serves as a diluent for the cyanuric acid units and to increase solubility of all copolymers in nonpolar solvents.[26] Hydrogen-bonded cross-linking was carried by employing either ditopic 2,4-diaminotriazine

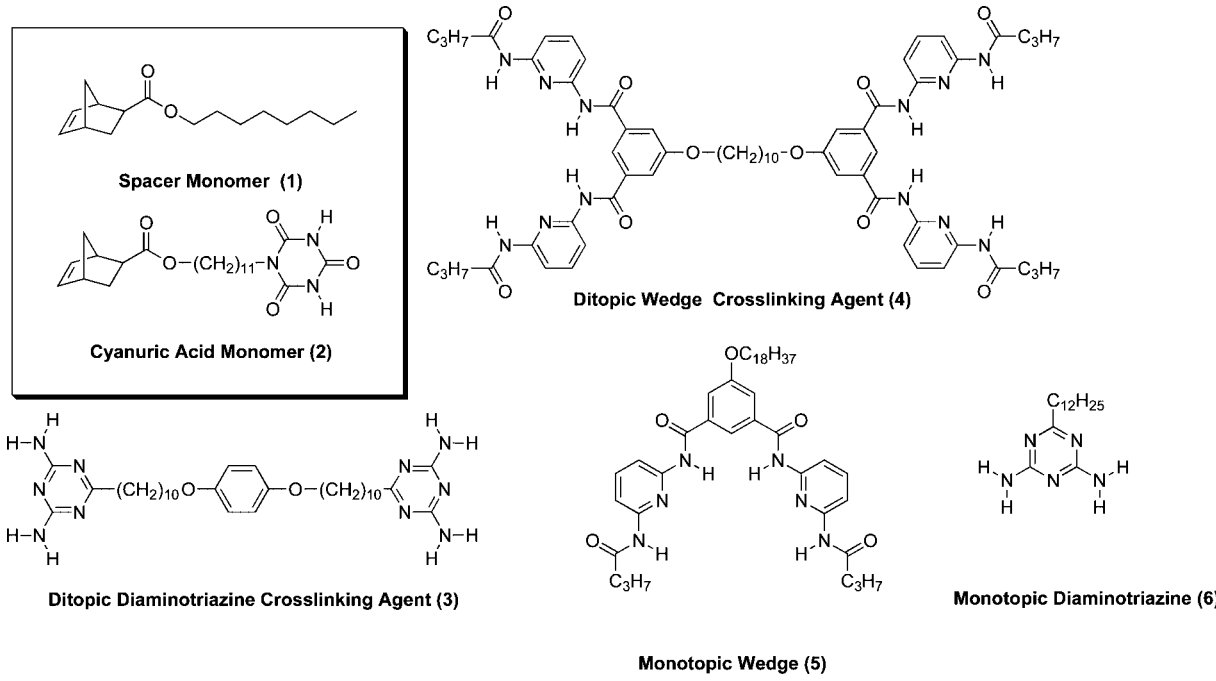
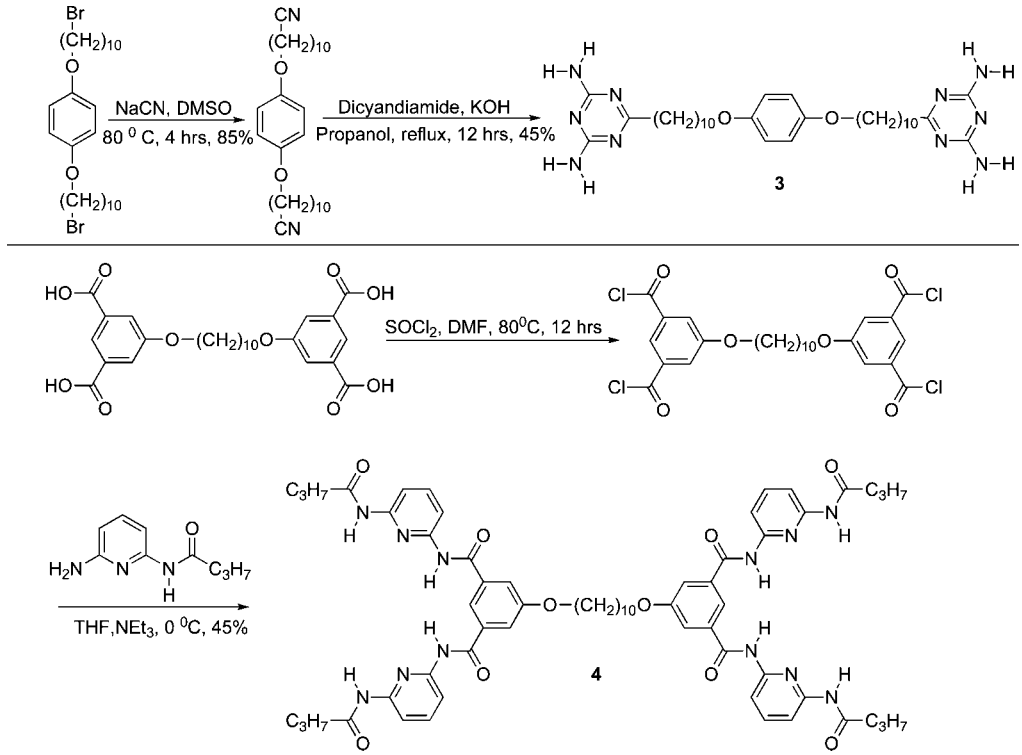


Figure 2. Monomers **1** and **2**, ditopic cross-linking agents **3** and **4**, and monotopic functionalizing agents **5** and **6** utilized in this study.

Scheme 1. Synthesis of Ditopic 2,4-Diaminotriazine Cross-Linking Agent (3) and Ditopic Hamilton Wedge Cross-Linking Agent (4)



(cross-linking agent **3**) or ditopic Hamilton wedge receptors (cross-linking agent **4**). All cross-linking events as well as all characterizations of the resulting cross-linked polymer networks were carried out in 1-chloronaphthalene, which is a noncompetitive, high boiling solvent in which all copolymers have good solubility. All monomers and cross-linking agents are shown in Figure 2. Monotopic agents **5** and **6** were used as model compounds to study the hydrogen bonding self-assembly.

Results and Discussion

Monomers **1** and **2** were synthesized according to literature procedures.[26,38] The ditopic 2,4-diaminotriazine cross-linking agent **3** was synthesized from 1,4-bis(10-bromodecyloxy)benzene in two steps as outlined in Scheme 1. 1,4-Bis(10-bromodecyloxy)benzene was treated with excess NaCN in DMSO to give 11,11′-(1,4-phenylenebis(oxy))diundecanenitrile in high yield requiring no subsequent purification. The corresponding dinitrile was then treated with dicyandiamide in propanol in the presence of KOH to give **3**, which was purified by repeated crystallizations from ethanol.[49]

Cross-linking agent **4** was also obtained in two steps. First, the tetra-acid was converted to its corresponding acid chloride derivative by refluxing it in excess thionyl chloride. After

Scheme 2. Synthesis of Poly-12 via ROMP Using Grubbs' First Generation Initiator

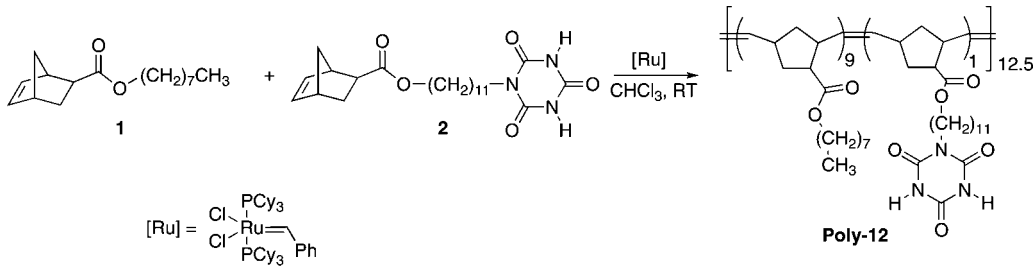


Table 1. GPC Data of Poly-12 Using THF as the Eluent[a]

entry	[M]/[I]	M_n (10^{-3})	M_w (10^{-3})	PDI
Poly-12	125	33	43	1.29
	250	88	101	1.15
	500	105	123	1.17

[a] The polymer structure is described in Scheme 2.

distilling off the thionyl chloride, the resulting tetra-acid chloride was immediately coupled with an excess of *N*-(6-aminopyridin-2-yl)butyramide in anhydrous THF and triethylamine at 0 °C. After stirring the reaction at ambient temperatures for 12 h, the solvent was removed under reduced pressure, and the residue suspended in ethyl acetate and filtered. Cross-linking agent **4**, which is insoluble in ethyl acetate, was isolated and purified by repeated washings with water to remove any triethylamine salts, followed by repeated washing with ethyl acetate to remove the excess amine.

Copolymerization Studies. We have previously reported the detailed polymerization behaviors of monomers **1** and **2**.[26,38] Both monomers can be copolymerized in a statistical manner via ROMP in chloroform at room temperature using Grubbs' first generation initiator (Scheme 2). We obtained complete monomer conversions within 3 h. The molecular weights of the polymers were easily controlled by the monomer-to-initiator feed ratios [M]/[I]. The highly controlled ROMP copolymerization of these monomers resulted in copolymers with controlled molecular weight and low polydispersities. Table 1 lists the gel-permeation chromatography characterization of these polymers.

Copolymer composition and molecular weight are two important parameters that affect the subsequent preparation of homogeneous cross-linked polymer networks in 1-chloronaphthalene, which was the solvent of choice for all our rheological measurements because of its relatively high boiling point. The solubility of all copolymers in 1-chloronaphthalene was found to depend on the mole fraction of **2**. Copolymers containing less than 20 mol % of **2** were completely soluble in nonpolar solvents, such as chloroform, while increasing the content of **2** above 20 mol % resulted in phase separation. In contrast, copolymers containing more than 20 mol % of **2** were fully soluble in polar solvents such as THF and DMF. The limited solubility in nonpolar solvents might be attributed to self-association of the cyanuric acid groups along the polymer backbone, which has been reported previously.[50] The copolymer composition for our rheological measurements was chosen to be 10 mol % of **2**, resulting in copolymers that were completely soluble in 1-chloronaphthalene.

The ability to prepare homogeneous cross-linked samples in solution was also found to be affected by molecular weight. We synthesized **Poly-12** with degrees of polymerization (DP) ranging from 100 to 1000. Above a DP of 500, all copolymers exhibited a tendency to undergo phase separation in 1-chloronaphthalene at concentrations of 5−10 wt %, which we again attributed to self-association of pendant cyanuric acid groups. Lowering the degree of polymerization to 250 allowed us to obtain uniform polymer solutions with a polymer concentration of 5−10 wt %. However, the addition of cross-linking agents still resulted in phase separation during network formation due to syneresis. Therefore, copolymers with a degree of polymerization of 125 were used for all rheological characterizations because they exhibited excellent solubility in 1-chloronaphthalene at polymer concentration of 10 wt % and formed homogeneous, stable polymer networks upon cross-linking.

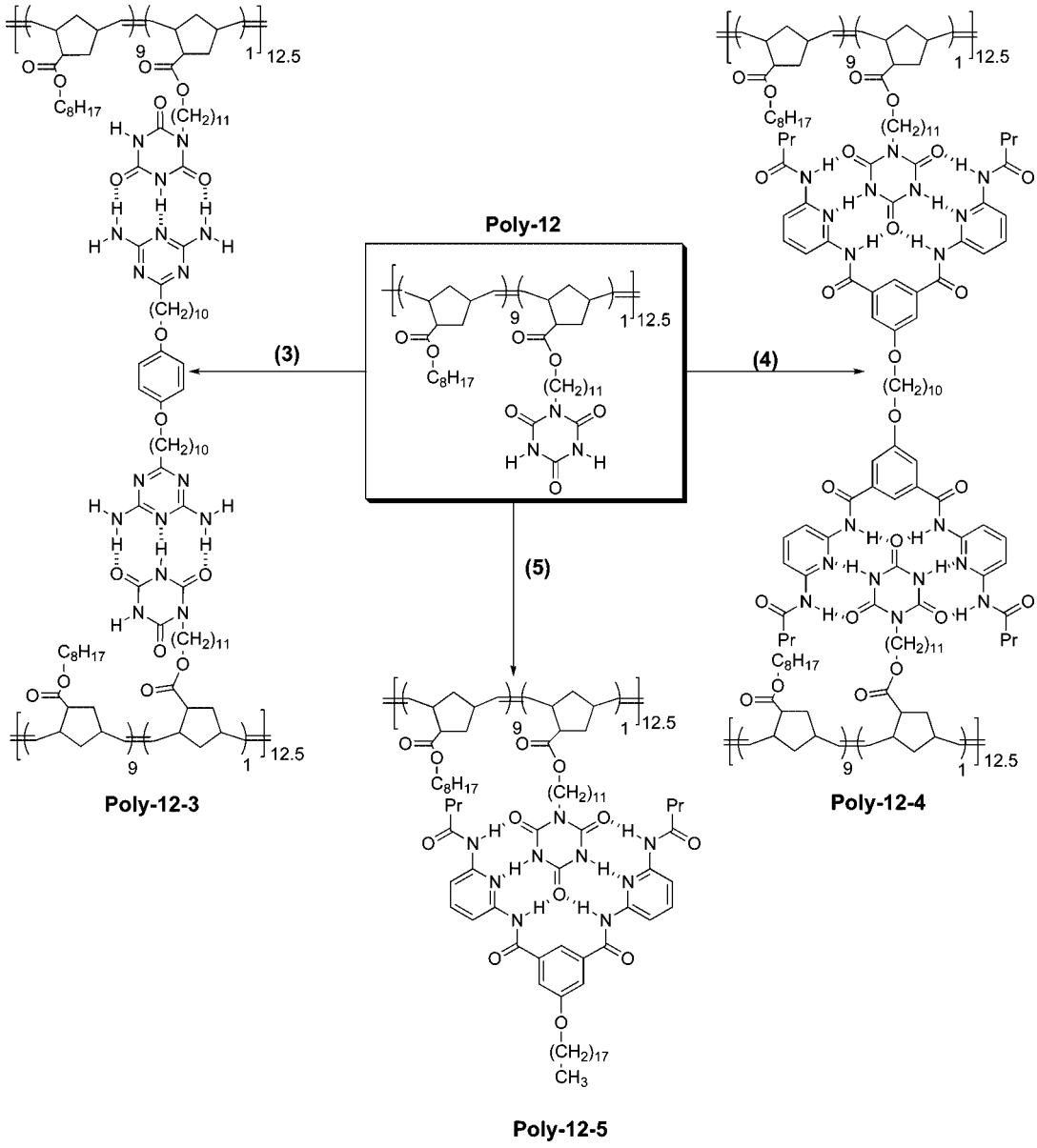
Self-Assembly and Cross-Linking Studies. Before conducting cross-linking studies, we first investigated the hydrogen bonding self-assembly between **2** and the monotopic compounds **5** and **6**, using ^{1}H NMR spectroscopy by monitoring shifts of the amine proton signal of **6**, the amide proton signals of **5**, and the imide proton signal of **2** both before and after self-assembly. These self-assembly experiments were performed using a 0.2 M solution of the compounds in deuterated chloroform. Upon the addition of 2 equiv of **6**, the imide signal of **2** shifted downfield from 9.57 to 13.60 ppm while the amine proton signals of **6** shifted downfield from 5.58 to 5.76 ppm. Further addition of another 2 equiv of **6** resulted in the downfield shifts of the imide protons of **2** to 13.77 ppm and the amine protons of **6** to 5.85 ppm.

The imide signal of **2** shifted downfield from 9.57 to 12.44 ppm upon the addition of 1 equiv of **5**, while the amide proton signals of **5** shifted downfield from 8.93 and 8.40 ppm to 9.85 and 9.53 ppm, respectively. Further addition of another equivalent of **5** resulted in a further downfield shift of the imide proton of **2** to 13.19 ppm and an upfield shift of the amide protons of **5** to 9.50 and 9.08 ppm. Similar results were obtained when copolymer **Poly-12** was self-assembled with **5** and **6**. These results demonstrate the strong hydrogen bonding interactions between monomer **2** and copolymer **Poly-12** with **5** and **6**.

After conducting these preliminary self-assembly studies we proceeded to cross-link **Poly-12** through hydrogen bonding self-assembly, using ditopic cross-linking agents **3** and **4** (Scheme 3).

The degree of cross-linking can be controlled easily via the amount of the cross-linking agent added. We varied the cross-linking agent concentration from 0% to 400% (molar ratio of functional groups in the cross-linking agent to cyanuric acid groups attached to the polymer chains). The cross-linked networks were characterized quantitatively using rheology, but initial visual observations of the mechanical properties provided a telling qualitative picture. While solutions of **Poly-12** yielded a low-viscosity fluid that readily flowed after vial inversion (center vial in Figure 3), cross-linking **Poly-12** with **3** resulted in an elastic solid. The left vial in Figure 3 shows the vial-inversion experiment for a 100% cross-linking agent concentration; the gel did not flow even after several months at room temperature. In contrast, when **Poly-12** was cross-linked with **4** at 100% cross-linking agent concentration, a highly viscous fluid was obtained. The right vial in Figure 3 shows this sample: although **Poly-12**−**4** initially passed the vial inversion test (i.e., no flow was detected for several minutes), gradual flow was observed after a period of several hours at room temperature, indicative of a highly viscous liquid. The marked difference in flow behavior is indicative of different self-assembled micro-

Scheme 3. Noncovalent Cross-Linking and Functionalization Strategies for Poly-12[a]



[a] (i) Network **Poly-12-3** via the addition of cross-linking agent **3**, (ii) network **Poly-12-4** via the addition of cross-linking agent **4**, and (iii) functionalized **Poly-12-5** via the addition of the monotopic functionalization agent **5**.

structures of the cross-linked materials. At first sight, it seems counterintuitive that the three-point cross-linking agent **3** results in an elastic gel, while the stronger six-point cross-links with agent **4** result in a high-viscosity fluid. In order to quantitatively probe the effect of both cross-linking agents on network formation, we carried out rheological measurements with a cone-and-plate rheometer.

Rheological Characterization. Initially, we investigated the presence of self-association of the cyanuric acid group in the un-cross-linked **Poly-12**. This study was important to determine whether there is any appreciable rheological effect due to self-association of the cyanuric acid functional groups. We compared the rheology of the pure polymer solution **Poly-12** with a control sample that also contained monotopic agent **5**. Compound **5** is designed to cap the cyanuric acid groups along the polymer backbone via Hamilton wedge six-point interaction and thus suppresses self-association of the cyanuric acid groups. Both with and without **5**, the polymer solutions behaved as viscous fluids with complex viscosities η^* of 0.06 Pa·s (without **5**) and 0.07 Pa·s (with **5**), respectively. The slight increase in viscosity after addition of **5** can be attributed to the strong association of **5** with the copolymer, which creates a bulkier polymer chain. Most importantly, the experiment indicates that there is no significant contribution from self-association of the cyanuric acid groups to the sample rheology. Hence, **Poly-12** can be seen as a cyanuric acid functionalized polymer that is suitable for cross-linking by using complementary hydrogen bonding interactions.

We next probed the mechanical properties of the cross-linked networks. The strain amplitude sweeps of **Poly-12−3** and **Poly-12−4** are shown in Figure 4. In both samples, the polymer concentration is 10 wt % and the cross-linking agent concentration 100%. It can be seen that for **Poly-12−3** the elastic modulus G' is greater than the loss modulus G'', indicating the formation of a gel according to a more stringent, quantitative rheological criterion than the qualitative vial inversion test in Figure 3. The gel breaks down at strain amplitudes larger than 0.1. In contrast, for **Poly-12−4** G'' is significantly greater than G' and largely insensitive to strain amplitude, indicating that the addition of

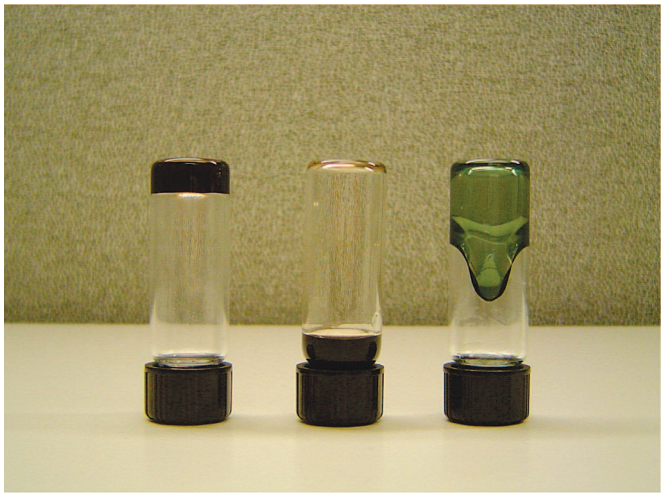


Figure 3. Optical micrograph of inverted vials 3−4 h at room temperature after vial inversion with (left) the stable elastic gel **Poly-12−3**, (center) the pure un-cross-linked **Poly-12**, and (right) the cross-linked viscous liquid **Poly-12−4**. All polymers and additives were dissolved in 1-chloronaphthalene.

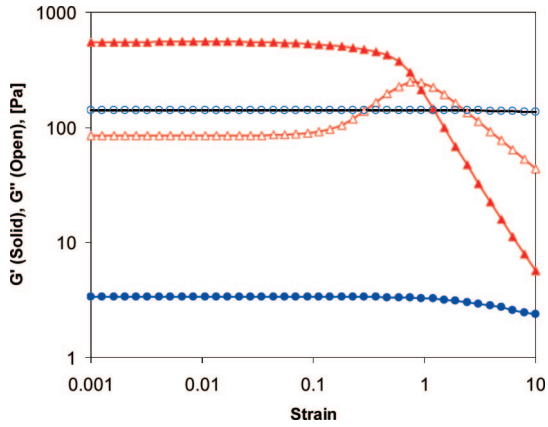


Figure 4. Strain amplitude sweep at 20 °C at $\omega = 6.3$ rad/s for **Poly-12−3** (triangles) and **Poly-12−4** (circles).

cross-linking agent **4** increases the viscosity of the network but does not result in the formation of a true viscoelastic gel.

In order to probe the thermal reversibility of the polymer networks, 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. During both the heating and cooling cycle the viscoelastic moduli were monitored at constant frequency (6.28 rad/s) and strain amplitude (0.1). At high temperatures, this protocol can lead to somewhat noisy data because the weak gels and low-viscous fluids yield low torques that are close to the sensitivity limitations of the rheometer.

The temperature sweeps in Figure 5 show a strong temperature dependence of the network. Both samples showed large gradual decreases of the dynamic moduli over the temperature range without sharp transitions. The decrease in moduli of both cross-linked systems (by a factor of ∼100) is much larger than temperature-related changes in viscosity for the pure solvent (1-chloronaphthalene), which decreases from 0.0028 to 0.0013 Pa•s over the same temperature range, and can thus be attributed to the breakup of hydrogen bonded intermolecular associations. The cross-linking in **Poly-12−3** is sufficiently stable that the network behaves as a viscoelastic gel even at 80 °C, as can be concluded from the fact that $G' > G''$ over the entire range in

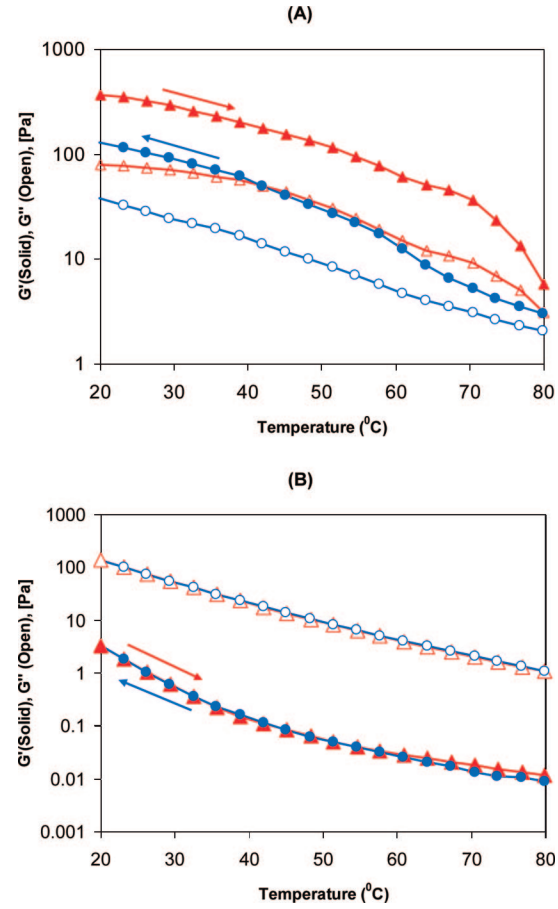


Figure 5. Temperature sweep profile: (A) **Poly-12−3** and (B) **Poly-12−4**. The red curves (triangles) denote the heating curves from 20 to 80 °C. The blue curves (circles) denote the cooling curves from 80 to 20 °C. G' and G'' were measured at $\omega = 6.3$ rad/s and strain amplitude 0.1.

Figure 5A. The recovery of these gels after cooling is also markedly different. Both samples show reversible increases of the moduli during the cooling cycle, although **Poly-12−3** exhibits significant hysteresis, while the viscous **Poly-12−4** recovers almost quantitatively.

To probe the thermal recovery and rheological behavior at high temperatures in more detail, we also conducted three frequency sweeps at constant strain amplitude: the first frequency sweep was conducted at 20 °C, the second at 80 °C after heating, and the third at 20 °C after the sample was cooled and allowed to rest for 20 min. The results are presented in Figure 6 for both cross-linking agents. From the frequency plots it can be seen that **Poly-12−3** indeed shows the behavior of a typical viscoelastic gel even at 80 °C, with $G' > G''$, while **Poly-12−4** predominantly exhibits viscous behavior. The figure also reiterates the effect of thermal history. After completion of the heating and cooling cycle, **Poly-12−3** exhibits a loss in both G' (∼40%) as well as in G'' (∼55%), whereas **Poly-12−4** shows quantitative recovery of both G' and G''; this effect was also noticeable as the hysteresis in Figure 5. Careful analysis of the rheological data in Figures 5 and 6 shows that after the cooling is completed **Poly-12−3** slowly recovers to its original strength: G' at 6.3 rad/s is only ca. 130 Pa at the end of the cooling cycle but recovers to ca. 210 Pa during the 20 min resting period. We hypothesize that the lack of polymer mobility in the cross-linked gel (**Poly-12−3**) hinders the recovery of the mechanical properties after cooling in comparison to the viscous liquid **Poly-12−4**. Although Figure 6 does not show a complete study of the temperature-dependent frequency sweeps, which

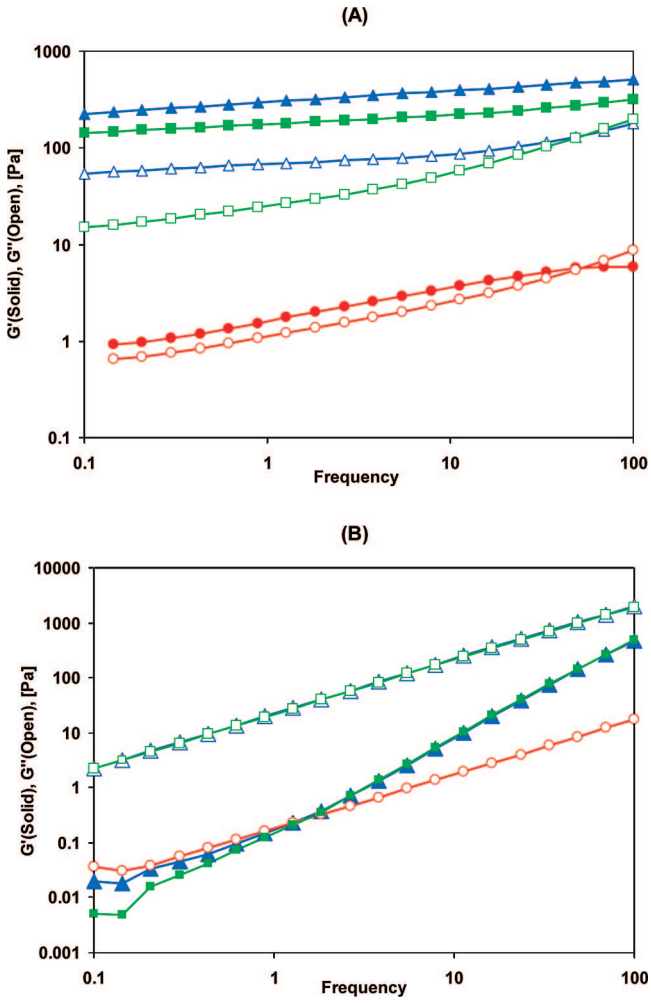


Figure 6. Frequency sweep profile: (A) **Poly-12−3** and (B) **Poly-12−4**. First sweep at 20 °C (triangles), second sweep at 80 °C (circles), and third sweep at 20 °C (rectangles), at strain amplitude 0.1. G' data for **Poly-12−4** at 80 °C has been omitted because of insufficient rheometer sensitivity.

was beyond the scope of our study, the limited data at 20 and 80 °C unambiguously shows that time−temperature superposition (TTS) is not applicable to **Poly-12−3**; it is not possible to overlap both moduli by simply shifting the frequencies. Because **Poly-12−4** is a viscous liquid, TTS of G'' is possible, but of limited scientific value.

The key hypothesis behind this research was that the use of complementary hydrogen bonding interactions for cross-linking allows for the fine-tuning of the degree of cross-linking and ultimately the materials properties through changes in the amount of the cross-linking agent added. In order to study this tunability, we investigated the cross-linking profile of our system by varying the concentration of **3** or **4**. An un-cross-linked solution of **Poly-12** was used as baseline for these experiments.

Figure 7 displays the cross-linking profile of **Poly-12−3**, in which the elastic and the loss moduli of **Poly-12−3** are plotted as a function of cross-linking agent concentration, again defined as the ratio of the molar concentration of functional groups in **3** to the molar concentration of cyanuric acid functional groups on **Poly-12**. The graph can be divided into two distinct regions, below 60% the sample is a viscous liquid with $G' < G''$, whereas at concentrations above 60% the sample displays predominantly elastic behavior with $G' > G''$. The concentration of 60% can be termed crossover or gelation concentration, since the elastic modulus becomes greater than the loss modulus and elastic gel-like properties are observed.

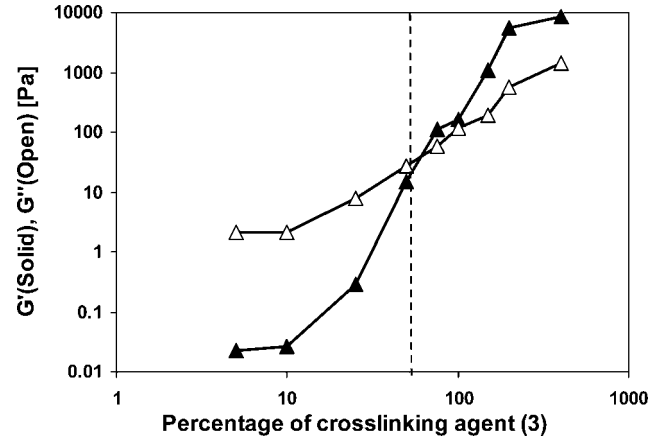


Figure 7. Cross-linking profile of **Poly-12** using **3**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at strain value of 0.1. The percentage of **3** is based on the molar ratio to cyanuric acid groups attached to the polymer.

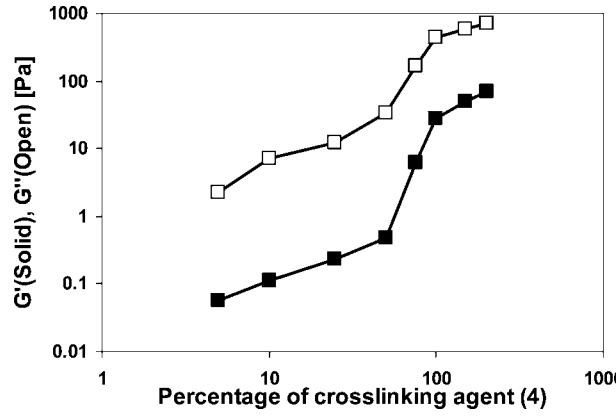


Figure 8. Cross-linking profile of **Poly-12** using **4**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at strain value of 0.1. The percentage of **4** is based on the cyanuric acid groups attached to the polymer.

Figure 8 displays the cross-linking profile of **Poly-12−4**. In contrast to Figure 7, it can be seen that G'' stays higher than G' over the entire concentration range; i.e., no elastic behavior is observed. Nevertheless, **4** is an efficient cross-linking agent, since the loss modulus reaches even higher values for than the elastic modulus found at analogous concentrations of **3**.

Clearly, there is marked difference in rheological nature of these two networks. The rheological data suggest that the addition of **3** results in the formation of a true sample-spanning network structure that is capable of bearing stresses, while **4** leads to cross-linking of several polymer chains without the high level of connectivity that characterizes a gel. Because of higher interaction strengths of the individual six-point hydrogen bonded complex between Hamilton wedge and cyanuric acid ($K_a \sim 10^6$ M^{-1} in chloroform at room temperature)[15] in comparison to the three-point hydrogen bonded complex of cyanuric acid and 2,4-diaminotriazine, the difference in rheology cannot be attributed to a simple variation in dissociation time scales between cross-linking agent and polymer backbone, which could change the relaxation time scales of the network. Instead, the data suggest a difference in the microstructure of the networks. At first sight, there is no obvious reason because both cross-linking agents are ditopic. A closer inspection of the molecular structure of **Poly-12−3** in Scheme 3, however, shows a possible explanation for the observed rheology: each cyanuric acid residue could actually establish hydrogen bonding with two 2,4-diaminotriazine groups of different cross-linking agent molecules

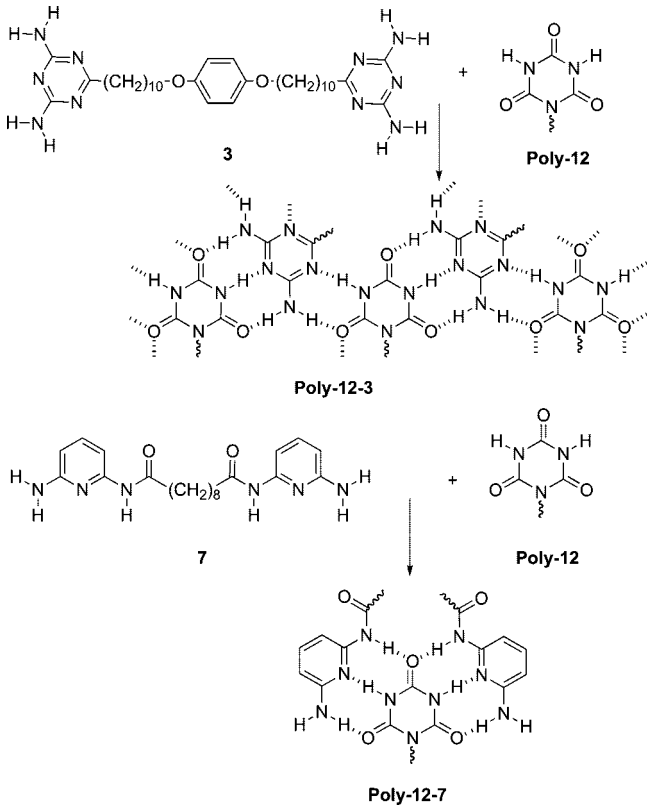


Figure 9. Proposed network microstructures for **Poly-12−3** and **Poly-12−7**.

(illustrated in Figure 9). As a result, each 2,4-diaminotriazine-based cross-linking agent **3** would potentially be connected to up to four cyanuric acid residues via two- and three-point hydrogen bonding, while the Hamilton wedge-based cross-linking agent **4** is limited to interactions with maximum two cyanuric acid residues. The resulting higher connectivity of **Poly-12−3** would explain the formation of a highly connected, sample-spanning network, while **Poly-12−4** consists of finite-size copolymer aggregates that significantly increase the solution viscosity but do not lead to gel-like properties. To test this hypothesis, we synthesized cross-linking agent **7** that is based on 2,6-diaminopyridine recognition units, which are very similar to the 2,4-diaminotriazine recognition unit but lack the two triazine nitrogen atoms. As a result, the addition of cross-linking agent **7** should result in a true three-point hydrogen bonding interaction with the cyanuric acid groups and multipoint array formation should not be possible. Indeed, it was found that the addition of cross-linking agent **7** to **Poly-12** resulted in free-flowing viscous liquids, even at the highest cross-linking agent concentration of 400 mol %. The drastic difference in behavior of **Poly-12−3** and **Poly-12−7** can be therefore attributed to the difference in the network microstructures: while **Poly-12−3** represents a true multipoint array network structure, **Poly-12−7** represents a point-to-point connected polymer network which does not have enough connectivity to form an elastic solid. The frequency plots of **Poly-12−3** and **Poly-12−7** at 100% respective cross-linking agent loading are illustrated in Figure 10, which shows that while **Poly-12−7** is a free-flowing liquid, **Poly-12−3** displays the characteristics of a highly connected, sample-spanning network.

Conclusions

In this contribution, we have synthesized random copolymers containing cyanuric acid recognition units via ROMP and investigated their cross-linking behavior via complementary

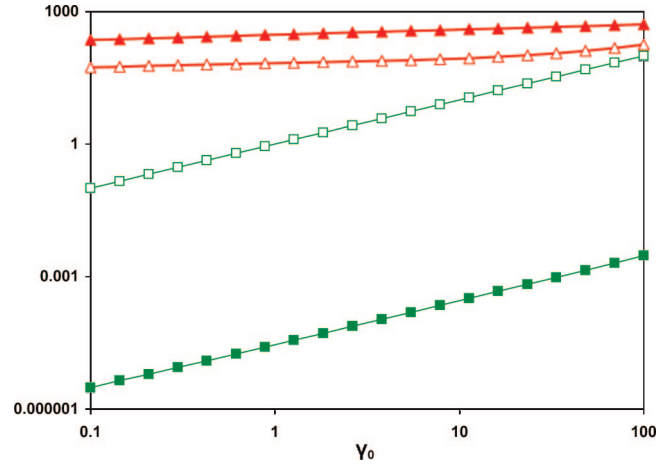


Figure 10. Frequency sweep profile at 20 °C: (A) **Poly-12−3** (triangles) and (B) **Poly-12−7** (rectangles) at strain amplitude 0.1.

hydrogen bonding in a nonpolar solvent, 1-chloronaphthalene. The hydrogen bonding recognition system consisted of the interaction between cyanuric acid units along the polymer backbone and small molecule ditopic cross-linking agents based on either 2,4-diaminotriazine or Hamilton wedge motifs. Our cross-linking system allows, by combining a functional group tolerant polymerization route with noncovalent cross-linking techniques, for the facile synthesis of reversible cross-linked polymers with a high degree of control over the extent of cross-linking and the network microstructure properties. Low-viscosity solutions of the parent copolymer could be changed into thermally reversible highly viscous liquids or elastic gels with tunable strength by simply varying the architecture and concentration of the cross-linking agent. Our approach results in the creation of materials with diverse mechanical properties from the same parent polymer backbone.

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