"Multi-functionalized Side-chain Supramolecular Polymers: A Methodology Towards Tunable Functional Materials"

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"MULTI-FUNCTIONALIZED SIDE-CHAIN SUPRAMOLECULAR POLYMERS: A METHODOLOGY TOWARDS TUNABLE FUNCTIONAL MATERIALS"

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For my best friend

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Å	angstrom
A	acceptor (in hydrogen bonding)
ATRP	atom transfer radical polymerization
^{13}C NMR	carbon magnetic resonance
^{o}C	degrees centigrade
cm^{-1}	wavenumber
δ	chemical shift
D	donor (in hydrogen bonding)
DAP	diaminopyridine
DCC	dicyclohexyl carbodiimide
DCM	dichloromethane
DMAP	4-dimethylamino pyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
DSC	differential scanning calorimetry
EI	electron ionization
EL	electroluminescence
ETL	electron transport layer
FAB	fast atom bombardment
FT-IR	Fourier transform infrared
g	gram

G′	elastic modulus
G″	loss modulus
GPC	gel permeation chromatography
h	hour
^{1}H NMR	proton nuclear magnetic resonance
HRMS	high-resolution mass spectroscopy
Hz	hertz
IR	infrared
J	coupling constant
Kcal	kilocalorie
L	liter
LC	liquid crystal
µL	microliter
M	molar
M^{+}	molecular ion
M^{-1}	inverse molar
m/z	mass-to-charge ratio
mg	milligram
MHz	megahertz
min	minute
mL	milliliter
mmol	millimole

M_n	number-average molecular weight
mol	mole
MsCl	methanesulfonyl chloride
M_w	weight-average molecular weight
NBT	*N*-butylthymine
NCN	nitrogen-carbon-nitrogen
NMR	nuclear magnetic resonance
OLED	organic light emitting diode
PCP	phosphorus-carbon-phosphorus
PDI	polydispersity index
POSS	polyhedral oligomeric silsesquioxane
ppm	parts per million
r.t.	room temperature
rad	radians
ROMP	ring-opening metathesis polymerization
s	second
SCFP	side-chain functionalized polymers
SCLCP	side-chain liquid crystalline polymers
SCMP	side-chain metal containing polymers
SCS	sulfur-carbon-sulfur
TTS	time temperature superposition
ω	angular frequency
%	percentage

SUMMARY

Even as we see a significant growth in the field of supramolecular polymers in the last ten years, multi-functionalized systems have been scarcely studied. Noncovalent multi-functionalization provides unique advantages such as rapid materials optimization via reversible functionalization as well as for the tuning of materials properties by exploiting the differences in the nature of these reversible interactions.

This thesis involves the design principles, synthesis & methodology of supramolecular side-chain multi-functionalized polymers. The combination of a functionally tolerant & controlled polymerization technique such as ROMP with multiple noncovalent interactions such as hydrogen bonding, metal coordination and ionic interactions has been successfully used to synthesize these polymers. Furthermore, the orthogonality between the above interactions in block/random copolymers has been studied in detail. It has been found that the studied interactions were orthogonal to each other.

To validate the viability of this methodology using multiple orthogonal interactions towards materials design noncovalent crosslinking of polymers has been used as a potential application. Three classes of networks have been studied: complementary multiple hydrogen bonded networks, metal crosslinked networks, & multi- functionalized hydrogen bonded and metal coordinated networks.

The first room temperature decrosslinking by exclusive complementary hydrogen bonded interactions has been successfully achieved. Furthermore network properties have been successfully tuned by varying the network micro-structure which in turn was tuned by the hydrogen bonding motifs used for inter-chain crosslinking.

By combining two different noncovalent interactions used for inter-chain crosslinking, it was possible to make multi-functionalized materials whose properties could be controlled by varying the crosslinking strategy. Hence by employing multi-functionalization methodology, important materials properties such as stimuli responsiveness can been tuned to yield novel materials which would be difficult to be obtained via traditional covalent chemistry or by using single noncovalent interactions.

CHAPTER ONE

Multi-functionalized Side-Chain Supramolecular Copolymers

1.1 Introduction

The combination of noncovalent chemistry and polymer science has lead to the emergence of the relatively new field of supramolecular polymer chemistry. In the past two decades this new area of science has seen a phenomenal growth mainly due to the significant advances in supramolecular and synthetic polymer chemistry. The synergy of these two areas of science has allowed for a quantum leap in supramolecular polymer science. Almost endless permutations and combinations of noncovalent interactions based on molecular recognition such as hydrogen bonding, metal coordination and Columbic interactions with a wide variety of polymeric scaffolds have been investigated with the goal to form highly functionalized complex nanoscale architectures and materials either by using single or multiple noncovalent interactions.

This introductory chapter will focus mainly on side-chain functionalized supramolecular polymers, specific advantages of side-chain functionalization over main chain functionalization, the advantages of multi-functionalization over mono-functionalization and finally some important application of side-chain functionalization methodology in the field of materials design. The design principles and the methodology of side-chain functionalization in particular multi-functionalization will be discussed in detail with examples in the published literature.

1.2 Side-chain supramolecular polymers

Supramolecular polymers can be defined as 'the formation of polymeric materials via noncovalent interactions using self-assembly' and can be categorized into main- and side-chain supramolecular polymers.[1] The vast majority of reports in the literature focus on main-chain supramolecular polymers (as shown in Figure 1.1) materials that are held together by noncovalent interactions such as hydrogen bonding, metal coordination or Columbic interactions.[2]

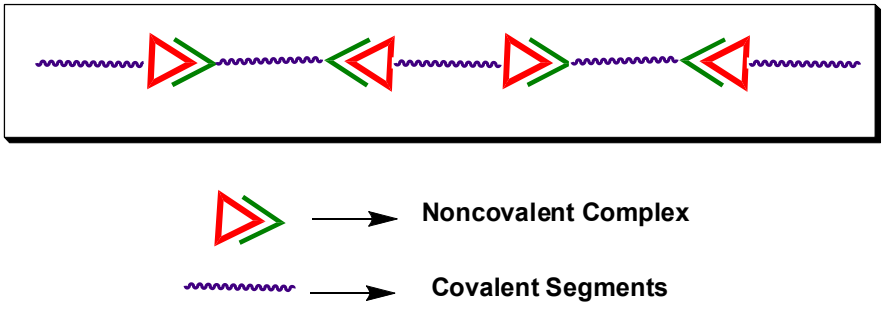


Figure 1.1 Cartoon representation of a generic main-chain supramolecular functionalized polymer.

Since the degree of polymerization and ultimately the stability of the polymer backbone are dependent upon the strength of the noncovalent interaction, main-chain supramolecular polymers often are limited to employing recognition motifs that have very strong binding efficiencies.

In contrast, side-chain supramolecular polymers are polymers in which the polymer backbone is based on covalent bonds (as shown in Figure 1.2) while the side-chains of the polymer are noncovalently functionalized.[3,4]

The main components of side-chain functionalized polymers are:

(i) polymer backbone,

(ii) side-chains,

(iii) noncovalent complex and

(iv) functional moiety.

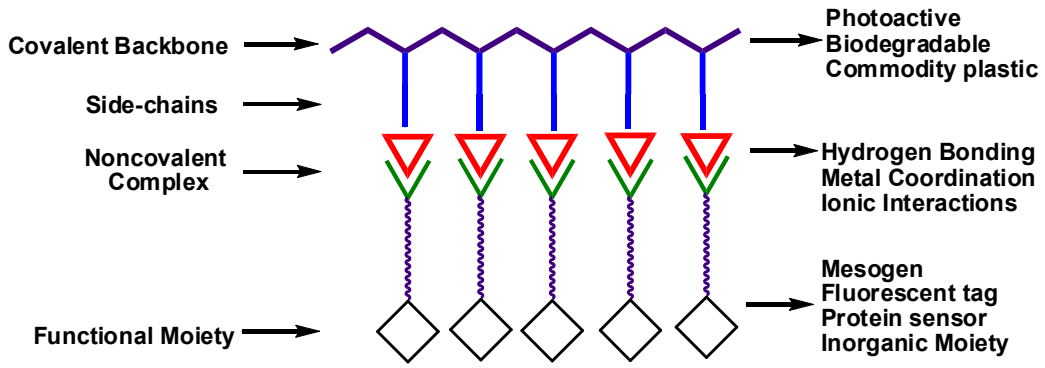


Figure 1.2 A cartoon representation of a generic side-chain supramolecular functionalized polymer.

(i) Polymer Backbone: The unique advantage of noncovalent side-chain functionalization is that it combines the robustness of the covalent main-chain polymer along with the reversibility and flexibility of noncovalent interactions, and hence has been used extensively in synthesizing "tailor-made" materials with controlled architectures and properties.[4] Depending upon the desired application, appropriate polymeric scaffold can be chosen from the vast number of extensively studied polymeric systems.[3] For example, copolymers such as random, alternating, di-, and tri-block as well as crosslinked polymeric networks, hyperbranched polymers, dendrimers, graft polymers have been employed as polymeric scaffolds for side-chain functionalization.[4] Furthermore, functional polymer backbones such as liquid crystalline polymer,[5] biodegradable polymers,[6] and lastly polymeric macrostructures such as vesicles, aggregates, networks and even inorganic materials such as nanoparticles have been utilized.[7]

(ii) Side-chains: Most side-chain functionalized polymers consist of long alkyl side-chains which tether the noncovalent recognition unit to the polymer backbone.[3] These side-chains act as a diluent, increasing the solubility of the polymers in different solvents, a specific advantage of processing considerations. The side-chains can also confer high solubility in specific solvents for the desired application. For example, the use of specific side-chains such as poly(ethyleneglycol) will result in highly water soluble system, where as the use of highly fluorinated side-chain segments will result in hydrophobic as well as lipophobic system. Furthermore, the presence of these side-chains also de-couples the motion of the polymer backbone from the noncovalent complex formation.

(iii) Noncovalent complex: The fundamental part of side-chain functionalized supramolecular polymers is the ability of fast reversible and facile functionalization. This functionalization can be achieved by using a noncovalent complex as a tethering point to reversibly attach the functional moiety of interest onto the polymer backbone. This tethering point is the heart of the system which consists of a noncovalent complex which is responsible for attaching the functional moiety of interest to the polymer backbone. Since the degree of polymerization and the stability of the polymer backbone are independent of the strength of the noncovalent interaction, a vast variety of interactions can be utilized in these systems, unlike in the previous main-chain systems. Hydrogen bonding, metal coordination, Columbic interactions, and dipole-dipole interactions are some of the most extensively employed noncovalent interactions used for side-chain functionalization of polymers.[8,3,4] By choosing the appropriate noncovalent interaction based on the association constant and desired responsiveness, quantitative functionalization of polymer scaffolds can be obtained. Furthermore in supramolecular

side-chain functionalized systems, the functional loading can be greatly controlled from a few mol% to 100% functional group loading. Such an extensive window for controlling the functional loading cannot be achieved in main-chain systems.

(iv) Functional moiety: A vast variety of functional moieties have been noncovalently and hence reversibly tethered to polymer backbones.[9-14] Furthermore just by altering the functional moiety the same polymer scaffold can be transformed into a family of functionalized "daughter-polymers" with vastly different properties and applications. Well known examples of functional moieties which have been used are fluorescent tags, bioactive molecules, photoactive molecules, mesogenic moieties, photoactive moieties, inorganic moieties etc.

Hence it can be seen that this strategy of using supramolecular side-chain functionalization offers an important advantage in the field of materials design, as by simply varying the desired noncovalent functionality self-assembled along a polymeric scaffold, a single parent polymer scaffold can be transformed into a family of functionalized polymers with very different and tunable physical and chemical properties. Therefore, this strategy is capable to circumvent lengthy sequential synthetic steps based on covalent chemistry and thus has the potential to allow for easier, faster and more efficiency materials optimization.

1.3 Synthetic strategies towards functionalized polymeric scaffolds

Side-chain functionalized polymers can be synthesized either by "pre-polymerization functionalization", i.e. the functionality has been bestowed to the monomer, or by "post-polymerization functionalization", after the polymerization, the polymer backbone is subsequently functionalized with the desired moiety. [3] While both

approaches have been employed successfully in covalent polymer chemistry, the first approach can be synthetically more demanding but always yields 100% functionalization which is not the case for most post-polymerization functionalization strategies.

In supramolecular side-chain functionalized polymers, the first functionalization strategy, the "pre-polymerization functionalization" is not always readily available. However, using appropriate design principles and noncovalent functionalization strategies, one can tune the "post-polymerization functionalization" strategy from fully functionalized polymers to very weak and non-perfect functionalized polymers, depending on the application in mind. Clearly, the strength of the noncovalent interaction in the desired medium is key to this strategy. Noncovalent interactions ranging the full spectrum of association constants from weak such as single point hydrogen bonding interactions, dipole-dipole, pi-pi stacking or hydrophilic interactions to fairly strong ones such as metal coordination or ionic interactions, have been used to functionalize polymeric scaffolds. It is important to note that the strength of these association constants is dependent on external factors such as the temperature and solvent. In the subsections below, the most common side-chain polymer functionalization strategies that are based on hydrogen bonding, metal coordination and ionic interactions will be discussed. These examples of noncovalent interactions to functionalize polymeric scaffolds along the side-chains are not meant to be conclusive but to demonstrate the basic design principles behind the functionalization strategies and to give some selected examples from the literature. Due to the vast number of examples of recognition motifs for the functionalization step that have been reported in the literature, it is beyond the scope of this chapter to mention all of them.

1.4 Synthetic aspects of side-chain functionalized polymers

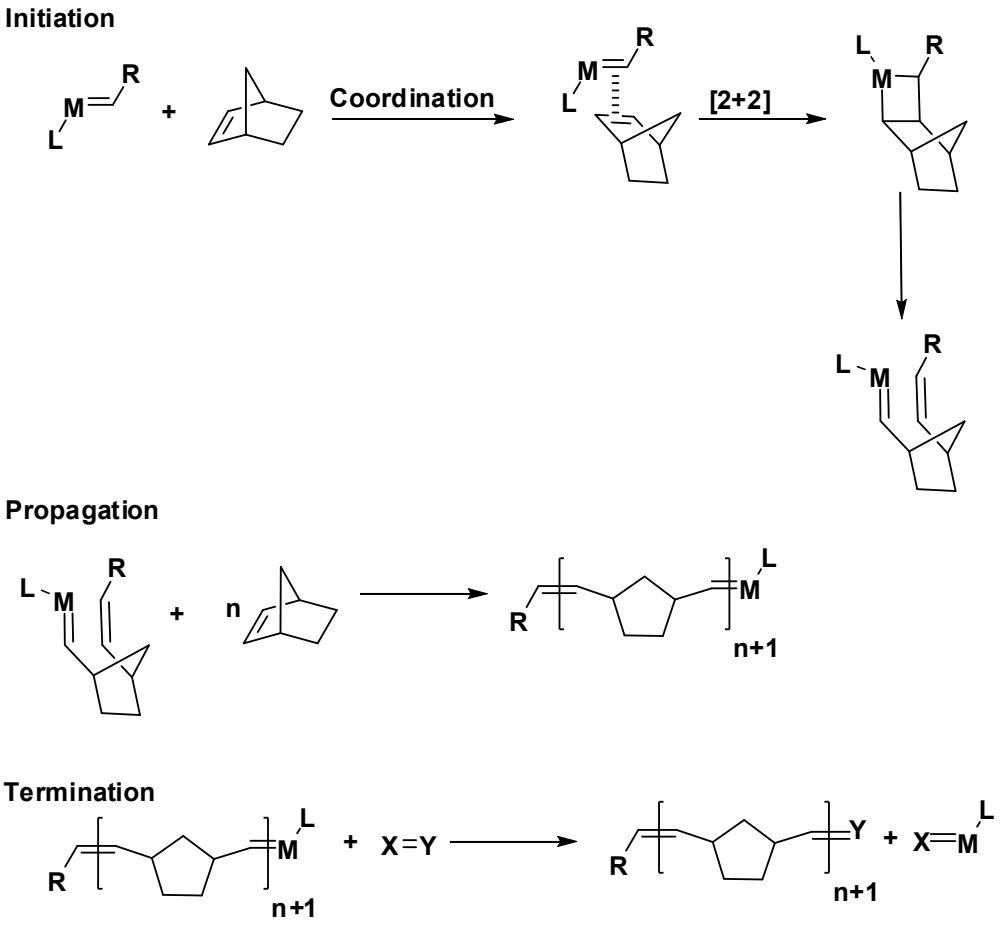
As described earlier, there are two main methods of synthesizing side-chain functionalized polymers, (i) polymerization of functionalized monomers (pre-polymerization functionalization) and (ii) polymer modification (post-polymerization functionalization).

Pre-polymerization functionalization: this method consists of polymerizing monomers which have been covalently functionalized with the noncovalent recognition functional group. The presence of highly electrophilic/nucleophilic centers requires that the polymerization technique employed must be sufficiently functional group tolerant. Traditionally, functionally tolerant techniques such as free-radical polymerization have been employed to polymerize functional monomers.[15] Although highly successful in synthesizing highly functionalized high molecular weight polymers, one of the most serious disadvantages of this polymerization technique is its uncontrolled polymerization nature. Hence the use of this technique essentially sacrificed the high control on the molecular architecture such as molecular weight and polydispersity index. Furthermore commercially important polymer classes with precise molecular architectures such as block copolymers were inaccessible using this technique. Well-established controlled polymerization techniques based on anionic polymerizations also could not be used due to presence of highly electrophilic/nucleophilic centers which prevent or interfere in the "controlled"/"living" polymerizations. Hence the options were generally restricted to either highly functionalized polymers with little control on the molecular architecture or unfunctionalized polymers with precise molecular architecture.

With the advent of functional group tolerant controlled polymerization techniques such as Ring-Opening Metathesis Polymerization (ROMP), allowed for the syntheses of highly functionalized polymers with a high degree of control on the macromolecular architecture.

1.4.1 *Ring-Opening Metathesis Polymerization (ROMP)*

ROMP is a transition-metal catalyzed polymerization method which is a subclass of olefin metathesis.[16] It involves a chain growth polymerization process in which cyclic olefins are converted to polymers. Since ROMP is based on olefin metathesis which involves a metal-mediated carbon–carbon double bond exchange process, the unsaturation associated with the monomer is retained in the final polymeric product. A general mechanism for ROMP, based on Chauvin's original proposal is shown in Scheme 1.1.



Scheme 1.1 A schematic representation of ROMP mechanism of norbornene illustrating the Chauvin pathway.

Initiation begins with the coordination of a transition metal alkylidene complex to a cyclic olefin. Subsequent [2+2]-cycloaddition produces a four-membered metallacyclobutane intermediate which effectively forms the beginning of a growing polymer chain. This intermediate undergoes a cycloreversion reaction to afford a new metal alkylidene. Although the resulting complex has increased in size, its reactivity toward cyclic olefins is retained as a result analogous steps are repeated during the propagation stage to yield the polymer. The termination can occur due to deactivation of the catalyst due to impurities, poisons or when deliberately quenched.

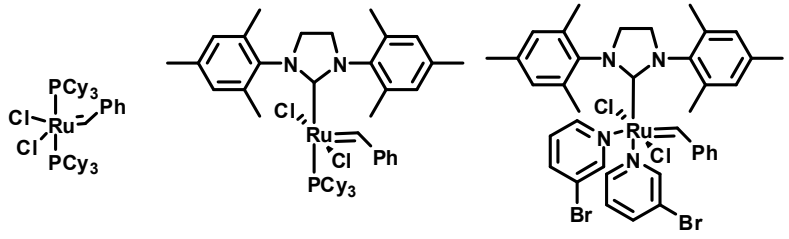
There are three important features of the metal-mediated ROMP reactions.

(i) the propagating metal centers on the growing polymer chains may exist in either the metallacyclobutane or metal alkylidene form,

(ii) like most olefin metathesis reactions, ROMP reactions are generally reversible. Thus, the basic mechanism illustrated in Scheme 1 can proceed in the opposite direction as shown and

(iii) though they are reversible reactions, these reactions are equilibrium-controlled and the position of the equilibrium can be predicted by considering the thermodynamics of the polymerization.

In ROMP the reaction is driven from monomer to polymer by the release of ring strain associated with the cyclic olefin balanced by entropic penalties. The common monomers used in ROMP are cyclic olefins which have a high degree of strain (45 kcal/mol) such as cyclobutene, cyclopentene, cis-cyclooctene, and norbornene. Modern initiators commonly employed in ROMP are based on molybdenum- and ruthenium-alkylidene transition metal complexes that were developed by Schrock[17] and Grubbs[16] respectively. In particular, Grubbs' initiators have enjoyed much utility due to their high functional group tolerance[18] and the ability to withstand the presence of air and water (Figure 1.3).



First Generation Initiator (A)

Second Generation Initiator (B)

Third Generation Initiator (C)

Figure 1.3 Grubbs' ruthenium alkylidene olefin metathesis initiators.

Living "controlled" ROMP: ROMP usually proceeds in a living "controlled" manner.[16] Living polymerizations give maximum control over molecular weight, composition, and polydispersity allowing for the formation of well-defined structures such as block copolymers. A ROMP reaction should exhibit the following characteristics in order to be considered ''living and controlled'':

(1) fast and complete initiation,

(2) a linear relationship between the degree of polymerization, measured as the number-average molecular weight of the polymer, (M_n) and monomer consumption,

(3) polydispersity index (PDI) around 1.5.

Hence to meet these requirements, the ROMP initiators should (1) enable complete, rapid initiation and complete monomer conversion to polymer (2) have negligible (intramolecular or intermolecular) chain-transfer or premature termination, (3) react with accessible terminating agents to facilitate selective end-functionalization, (4) display good solubility in common organic solvents, and (5) show high stability toward moisture, air, and common organic functional groups.[16]

Complete monomer conversion to polymer, results in well-defined polymers with narrow distributions and predictable molecular weights specified by the initial monomer to initiator ratio (M/I). Hence a "controlled living" ROMP reaction can be a route to synthesize well-defined block-, graft-, and other types of copolymers, end-functionalized polymers, and various other polymeric materials with complex architectures and useful functions. Coupled with the high functional tolerance,[19,20] ROMP can offer the advantage

of a high degree of control over the polymer architecture as well as high functionality, thus resulting in well-defined highly functionalized polymers.

1.5 Side-chain functionalization using hydrogen bonding interactions

Hydrogen bonding interactions are the most widely employed noncovalent interactions for the functionalization of polymeric scaffolds.[21, 22] Over the past 20 years, a wide variety of hydrogen bonding motifs ranging from single, two, three, four, and six-point recognition motifs to higher order systems have been developed. Figure 1.4 describes some of the more common recognition motifs described in the literature. The popularity of hydrogen bonding is due to the fact that the strength of the hydrogen bonded complexes can be tuned easily by using these different hydrogen bonding motifs and by altering the acidity and basicity of the donor (D) and acceptor (A) moieties respectively. By choosing the appropriate hydrogen bonding motif, binding constants (measured in a relatively nonpolar solvent such as chloroform at room temperature) as low as 1 M^{-1} for a single hydrogen bonding interaction to binding constants more than 10^6 M^{-1} for multiple hydrogen bonded interactions can be 'programmed'.[23]

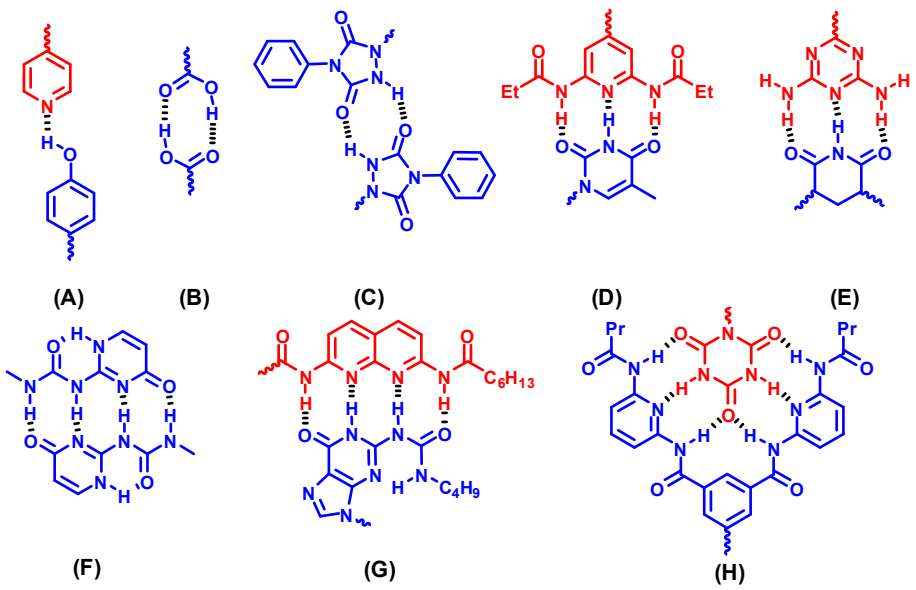


Figure 1.4 Examples of hydrogen bonding motifs that have been used in side-chain functionalizations of polymers: single point complementary (A), two-point dimerizing (B and C), three-point complementary (D and E), four-point dimerizing (F), four-point complementary (G), and six-point complementary (H) hydrogen bonding motifs.

Typically, in solution the hydrogen bonding interactions have a strength ranging between 10-120 KJ/mol (depending on the solvent) with an approximate range of length of 0.15 -10.0 nm.[24] All hydrogen bonding motifs can be categorized into two distinct classes: 1) self-dimerizing interactions in which the hydrogen bonding motifs have a high tendency of self-complexation, examples of such motifs are self-dimerizing carboxylic acid groups, urazole groups[13] and 2) complementary hydrogen bonding interactions in which the recognition motifs have a complementary recognition partner with which a stable complex formation is preferentially formed over self-complexation.[25] Examples of such complementary motifs are the recognition pair 2,6-diaminopyridine and thymine[8] (Figure 1.4, D) as well as cyanuric acid and the Hamilton wedge receptor[26] (Figure 1.4, H).

In general, self-assembly using hydrogen bonding interactions is especially facile requiring no prior activation as compared to other interactions such as metal

coordination. It consists of a simple "mix and stir" chemistry of the recognition unit involved. Since hydrogen bonding interactions are thermally reversible the strength of the interactions as well as the thermal responsiveness of the system can be controlled greatly. Figure 1.5 describes some examples from the literature of side-chain functionalized supramolecular scaffolds using hydrogen bonding. The importance of hydrogen bonding interactions can be judged from the vast number of examples reported in literature ranging from small molecule self-assembly[27] to self-assembled supramolecular polymers.[28, 4] The versatility and the ease of self-assembly of hydrogen bonding interactions have made it a popular choice in both main-chain[28] and side-chain supramolecular polymers.[3,4]

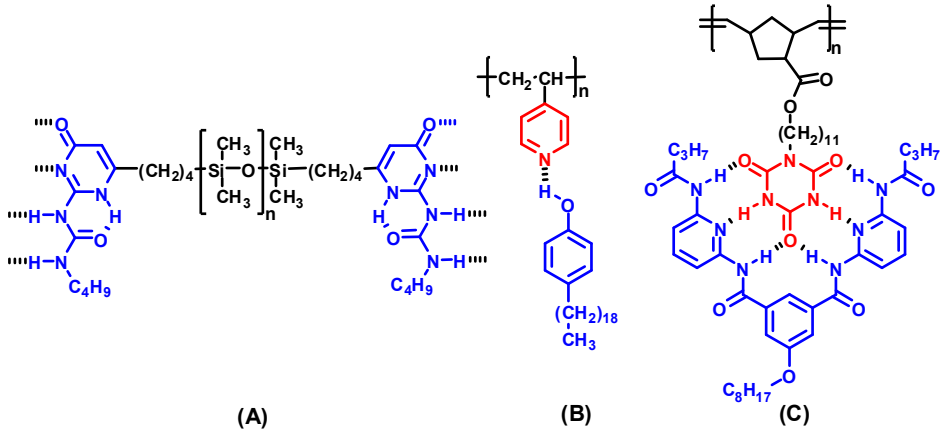


Figure 1.5 Examples of hydrogen bonding motifs that have been used in supramolecular polymers: dimerizing UPy functionalized main-chain supramolecular polymers (**A**), simple one-point complementary hydrogen bonding interactions between pyridine and phenol (**B**), and six-point complementary hydrogen bonding interaction between cyanuric acid and the Hamilton wedge receptor (**C**).

The groups of Weck[26] and Sleiman[29,30] have synthesized a variety of copolymers functionalized by either thymine or diaminopyridine derivatives or biological important groups such as biotin, adenine etc. using ROMP. Sleiman then investigated their self-

assembly into nanostructures – such as star micelles – using the hydrogen bonding moieties to control the formation of the three-dimensional structures.[29, 30]

Rotello and co-workers carried out "post-polymerization functionalization" of poly(styrene) copolymers containing randomly dispersed chloromethylstyrenes functional groups with 2,4-diaminotriazine or 2,6-diaminopyridine derivatives yielding poly(styrene) copolymers with terminal hydrogen bonding recognition moieties along the side-chains.[31] These scaffolds were then functionalized noncovalently using hydrogen bonding with a variety of small molecules including sesquiloxane to form inorganic-organic hybrid materials.[31] Such a strategy of obtaining a host of different materials from the same parent polymeric scaffold just by varying the anchoring moieties was named "Plug and Play Polymers" by the Rotello group.[31]

1.6 Side-chain functionalization using metal coordination

The second major class of noncovalent interactions that have been employed extensively in the literature for polymeric functionalization is metal coordination.[32-37] Side-chain metal functionalized polymers possess the characteristic properties of both, the metal and the polymer components, giving rise to a variety of hybrid materials thereby exhibiting metal-specific properties such as conductivity and magnetism while maintaining the benefit of solubility and processability due to the polymer backbone. These metal-ligand interactions are fairly temperature insensitive as compared to hydrogen bonding interactions. However, they are highly sensitive to ligand displacement reactions and are therefore considered to be chemoresponsive. Advantages of metal-complexes include their highly controlled synthesis, the formation of strong noncovalent bonds in non-competing solvents, the potential application of metal-

containing polymers in areas such as supported catalysis,[38] electro-optical materials,[39] and chemically responsive gels.[40]

Side-chain metal functionalized polymers fall into two classes according to the position of the metal complex with respect to the polymer backbone. In the first class, the metal is covalently tethered to the polymer backbone, whereas the complementary component, the ligand, is coordinated to the 'polymeric scaffold'. In the second class of side-chain metal functionalized polymers, the ligand is covalently attached to the polymer backbone to form a "polymeric ligand species" also often called a macroligand whereas the metal center is then subsequently complexed on to the polymer. In both cases, the resultant polymers may possess identical structures and the choice of the synthetic strategy is dependent on the ease of the synthetic method: the synthesis of polymeric ligand scaffolds is more facile as compared to the polymerization of a metal containing monomer due to the limited number of polymerization methods as a result of the metal intolerance of most polymerization techniques. Although many examples of side-chain metal coordinated polymers exist, only a few are designed to serve as recognition motifs for controlled side-chain functionalization. The two most widely encountered metal coordination recognition units in side-chain supramolecular polymers are palladated SCS pincer complexes[41-44] and metal-terpyridine/bipyridine complexes.[45,36]

Palladated sulfur-carbon-sulfur (SCS) pincer complexes are an important class in coordination chemistry and have been used widely ranging from catalysis[38] to anchoring units in functional materials.[36] They consist of a metallated tridentate pincer ligand having a square planar coordination sphere with only one chemically accessible coordination site for self-assembly with monodentate ligands such as nitriles, pyridines,

thiocyanates or phosphines. The stability of the metal ligand complex is in the order phosphine > pyridine > thiocyanate ~ nitrile.[46] Weck and co-workers reported the preparation of poly(norbornene)s bearing palladated SCS pincer complexes at every repeat unit which then could be functionalized with pyridines or nitriles (Figure 1.6 A).[44] In all cases, these polymers were formed via living polymerization methods allowing for low polydispersities and full stoichiometric control over the molecular weight.

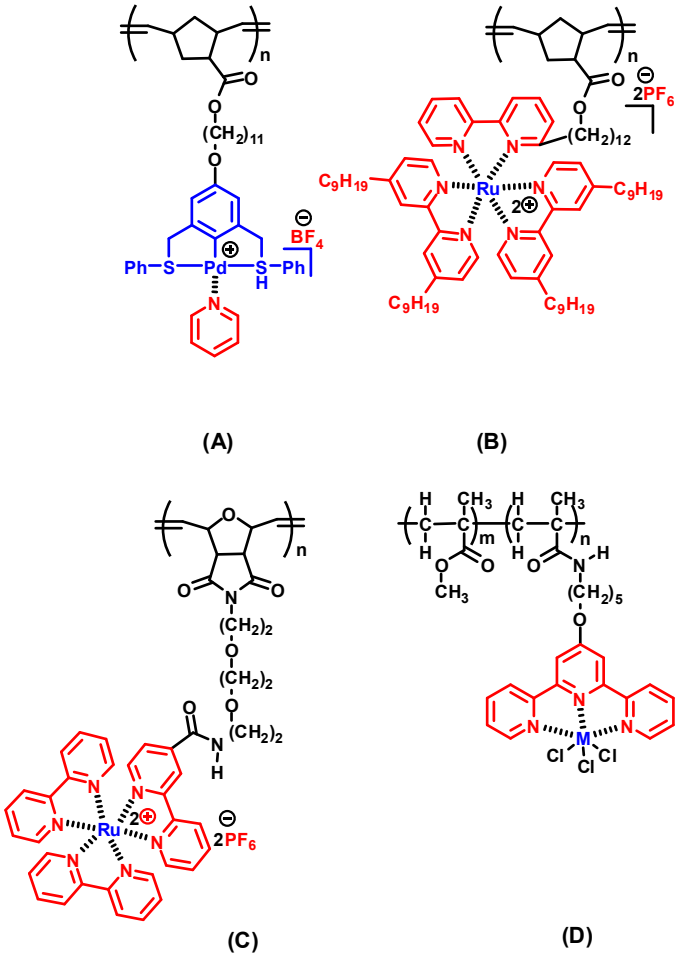


Figure 1.6 Examples of metal coordination motifs employed for side-chain functionalization of polymers.

Metal-terpyridine/bipyridine complexes are the second class of common metal-ligand interactions used in side-chain functionalized polymers. The importance of these metal complexes lies in their electro/photoluminescent properties as well as the

possibility to direct self-assembly in supramolecular systems. Schubert and co-workers have extensively used terpyridine-based metal coordination for both side-chain and main-chain functionalization. [35] Tew and co-workers used a post-polymerization functionalization approach to covalently attach terpyridine functional groups on both random and block copolymers based on methacrylates that were copolymerized using atom-transfer radical polymerization.(Figure 1.6 D) Subsequent metal complexation of the terpyridine groups resulted in copolymers generating emissive materials in the blue, green, and red. [47] In contrast to the post-polymerization approach described by Tew and co-workers, [48] Weck and Carlise [33] have employed pre-polymerization functionalization, i.e. they reported the synthesis of a norbornene monomer functionalized with a Ru-bpy complex which was then subsequently polymerized using Grubbs' third generation catalyst leading to well-defined polymers with 100% functionalization (Figure 1.6 B). Although both these metal complexes have been used extensively in noncovalent polymer functionalization, the SCS-Pd pincer functionalization has the added advantage that the metal coordination requires very mild conditions in contrast to the metal complexation involving the terpyridine ligands.

1.7 Side-chain functionalization using Coulombic interactions

Coulombic interactions are among the most widely encountered noncovalent interactions in polymeric systems rivaled only by hydrogen bonding and van der Vaals interactions in their frequency.[49] The most important example of using Coulombic interactions in materials science is in the field of "ionomers" which are tailor-made materials. Ionomers are widely used commercially due to their unique physical properties such as enhanced impact strength, toughness and thermal reversibility.[50] Other

examples of Coulombic interactions in side-chain functionalized polymeric systems, include charged block copolymers,[51] crosslinked polymers using charge interactions,[52] self-assembled dendrimers,[53] Coulombically linked side-chain liquid crystalline polymers, and Coulombic polyamphiphiles amongst others.[54] The polymeric scaffold can either be positively or negatively charged, hence can be considered to be a "polyelectrolyte". The majority of the Coulombically functionalized side-chain polymers are based on "post-polymerization" functionalizations to circumvent severe interference of the charged Coulombic centers during the synthesis. More recently, with the advent of highly functional group tolerant yet mild polymerization techniques such as ROMP, there have been reports of polymerization of charged monomers. For example, Lonergon and co-workers have reported the ROMP of both positively as well as negatively charged cyclooctatetraenes, using a tungsten- based Schrock catalyst (Figure 1.7 A and B).[55, 56]

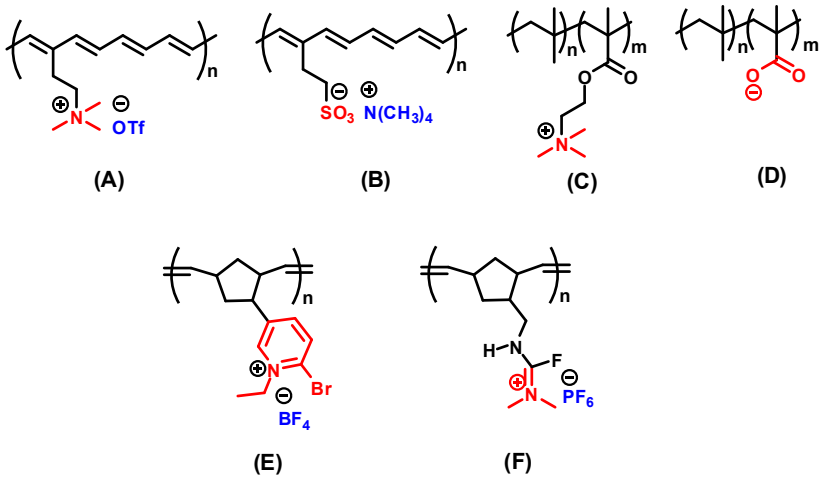


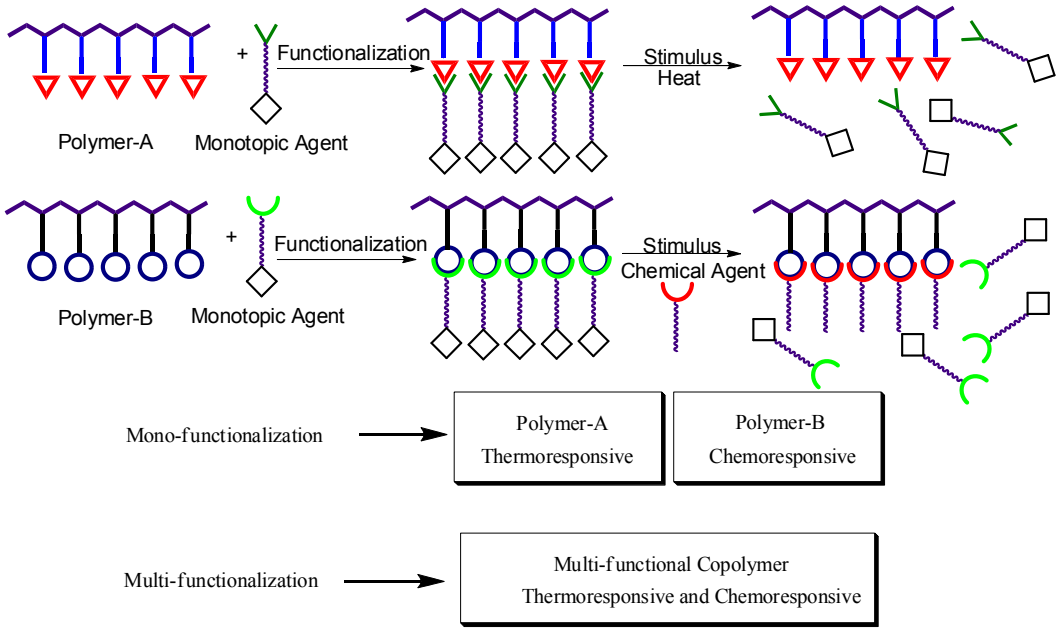
Figure 1.7 Examples of charged Coulombic moieties employed for side-chain functionalization of polymers.

Barrett and co-workers polymerized a positively charged norbornene monomer using Grubbs' second generation ruthenium initiator (Figure 1.7 F and G).[57] Unfortunately, the polymerizations of charged monomers are mostly uncontrolled preventing the easy formation of block copolymers. Kennedy and co-workers

circumvented this problem by using a post-polymerization method to introduce the charge species onto one or more blocks of block copolymers that were synthesized using ATRP. (Figure 1.7 C and 1.7 D).[58]

1.8 Noncovalent multi-functionalization of side-chains of polymeric scaffolds

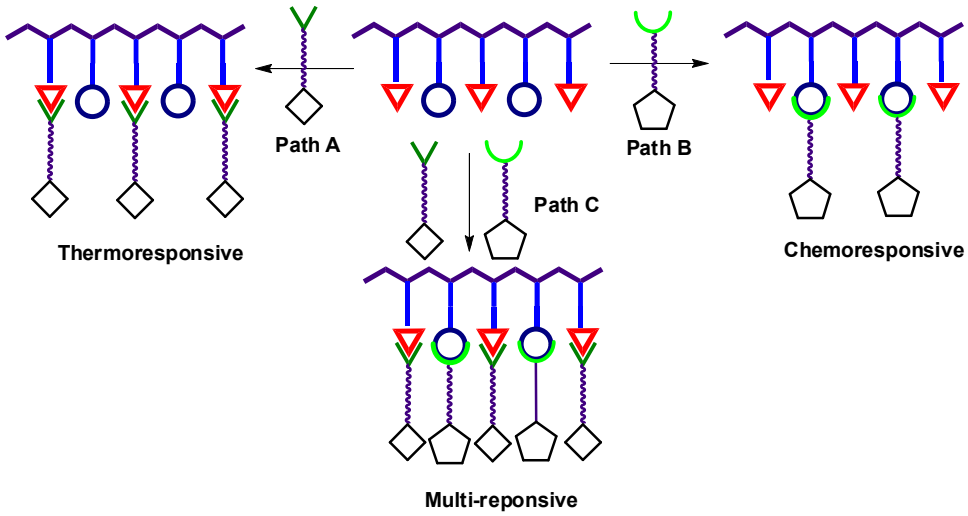
In the previous section, the supramolecular side-chain functionalization of polymers based on a single recognition motif was explained. The use of a single noncovalent interaction such as hydrogen bonding interactions for side-chain polymer functionalization results in material which exhibits only thermal responsiveness, as shown in Scheme 1.2.



Scheme 1.2 Concept of using side-chain multi-functionalization of polymers for synthesis of multi-responsive materials.

However, biological systems use a wide variety of noncovalent interactions such as hydrogen bonding, metal coordination, and hydrophobic interactions in an orthogonal fashion to introduce function, diversity, and complexity. Although most of the concepts

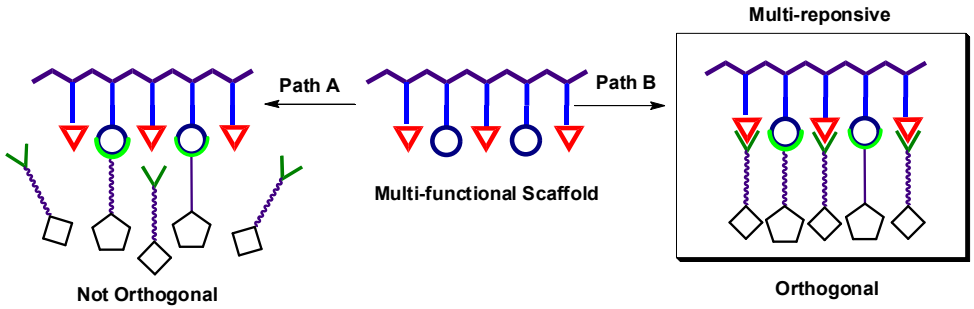
of supramolecular polymer science are inspired from self-assembly process in nature, the vast majority of supramolecular polymers are based solely on one molecular recognition motif. In the future, supramolecular side-chain functionalized polymers for advanced applications will require multiple functionalities combined with controlled architectures. Noncovalent multi-functionalized materials will provide unique advantages such as rapid optimization via reversible functionalization to give highly advanced materials whose responsiveness to external stimuli could be tuned. Such systems will open new possibilities for the preparation of dynamic and rapidly optimized ‘‘smart’’ materials.[59]



Scheme 1.3 Cartoon representation of stepwise multi-functionalization of a multi-functionalized polymer scaffold; using hydrogen bonding interactions (Path A), metal coordination (Path B) and multi-functionalization using hydrogen bonding and metal coordination (Path C).

One strategy for the noncovalent multi-functionalization of side-chain supramolecular polymers would be the controlled employment of multiple noncovalent interactions within the same polymeric system as shown in Scheme 1.3. Such a strategy should allow for the tailoring of materials properties by exploiting the differences in the nature of these reversible interactions as well as multi-functionalization. An important

prerequisite for the use of multiple interactions in such a system is that all noncovalent interactions must be orthogonal to each other (Scheme 1.4), or at least the effects of one interaction in the presence of another one must be clearly understood, such that multiple interactions can be simultaneously used with a high degree of control on the system.



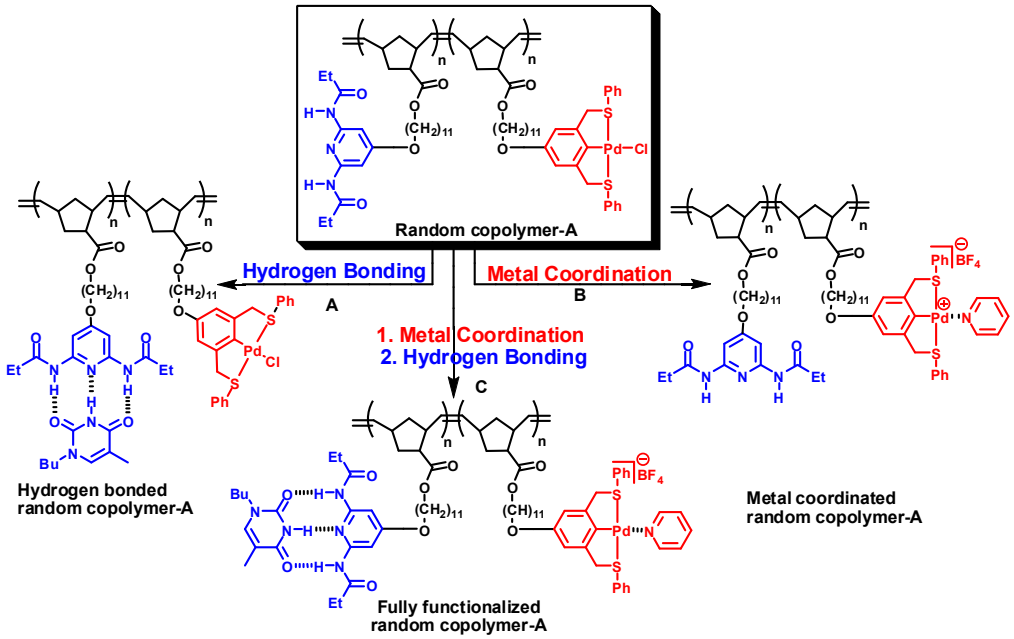
Scheme 1.4 Cartoon representation of orthogonal multi-functionalization in which both the noncovalent interactions are mutually independent of each other (Path B) and non orthogonal multi-functionalization in which metal coordination of the polymer scaffold disrupts the hydrogen bonding functionalization of the polymer scaffold (Path A).

The Weck group has demonstrated that a family of materials derived from a single polymer backbone can be prepared rapidly and quantitatively with desirable properties via an orthogonal multi-functional self-assembly approach.[43] Some of these examples in which the above strategy is used will be discussed below.

1.9 Combination of hydrogen bonding and metal coordination interactions

The Weck group was the first to establish the orthogonality of hydrogen bonding interactions and metal coordination in side-chain polymers.[43] The hydrogen bonding interactions employed were based on the three-point hydrogen bonding complex between 2,6-diaminopyridine and *N*-butylthymine whereas the metal coordination was based on palladated SCS pincer metal complex which were functionalized via coordination chemistry with pyridine or nitriles.[43] In order to measure the strength of the hydrogen

bonding interactions and to demonstrate the orthogonality of the two noncovalent interactions, the systems were characterized extensively using ^{1}H NMR spectroscopy. The initial studies involved random polymers based on poly(norbornene)s. They found that the strength of the hydrogen bonding interactions was independent upon the presence/absence of the metal coordinated sites. Furthermore the studied interactions were also independent upon the functionalization route used, i.e. metal coordination followed by hydrogen bonding, hydrogen bonding followed by metal coordination or all in one single step (Scheme 1.5).



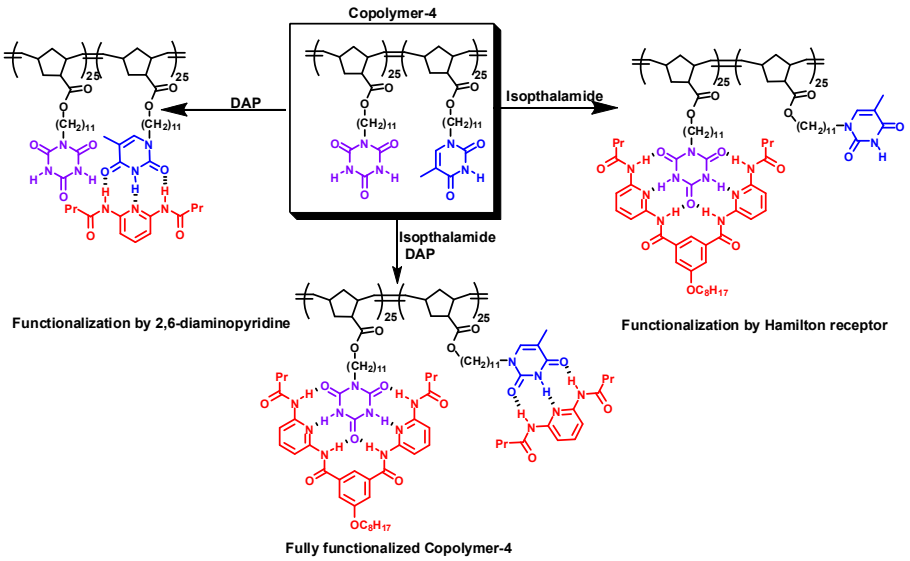
Scheme 1.5 Stepwise functionalization of multi-functional polymer scaffold based on random copolymer using hydrogen bonding and metal coordination interactions.

1.10 Multiple hydrogen bonding interactions: Self-sorting on polymers

The Weck group has also investigated the incorporation of multiple hydrogen bonding interactions along a single polymer backbone for random copolymers as shown in Scheme 1.6.[43] **Copolymer-4** based on poly(norbornene) was functionalized with two different hydrogen bonding side-chains based on thymine and cyanuric acid recognition

groups.[26] It was demonstrated that the thymine and cyanuric acid units were able to self-assemble with their complementary 2,6-diamimopyridine and Hamilton wedge moieties, respectively, even in the presence of competitive recognition sites. Hence selective functionalization of the copolymers can be accomplished by a one-step orthogonal self-assembly approach.

The selective self-assembly of a receptor molecule with its complementary recognition unit in the presence of a competitive recognition unit has been described as self-sorting in the literature. Using the above described system containing two hydrogen bonding units, Weck and Burd were able to prove for the first time the concept of self-sorting in synthetic polymers and suggest the design of complex polymeric materials containing competitive noncovalent interactions.[26]



Scheme 1.6 Functionalization strategies of **copolymer-4** based on multiple hydrogen bonding interactions.

1.11 Terpolymer functionalization strategies: Combining hydrogen bonding, metal coordination and pseudorotaxane formation

Random poly(norbornene)-based **terpolymer-5** (Figure 1.8) functionalized with sulfur-carbon-sulfur (SCS) palladated pincer complexes, dibenzo[24]crown-8 (DB24C8) rings, and 2,6-diaminopyridine units were synthesized by ROMP.[60] The palladium complex serves as anchoring unit for metal coordination, 2,6-diaminopyridine as DAD hydrogen bonding moiety, and DB24C8 as precursor for pseudorotaxane formation, which has been studied extensively by Stoddart and co-workers.[61] Side-chain functionalization of these terpolymers was achieved by self-assembling (i) pyridines to the palladated pincer complexes, (ii) dibenzylammonium ions to the dibenzyl-24-crown ether (DB24C8) rings, and (iii) thymine to the 2,6-diaminopyridine receptors. Again, by following the hydrogen bonding an as well as the pseudorotaxane formation by ^{1}H NMR spectroscopy and isothermal titration calorimetry, the Weck and Stoddart groups were able to demonstrate that the association constants were unaffected by neighboring functionalities on the polymer backbone, demonstrating for the first time orthogonality in the recognition expressed by three well-defined and discrete recognition sites.

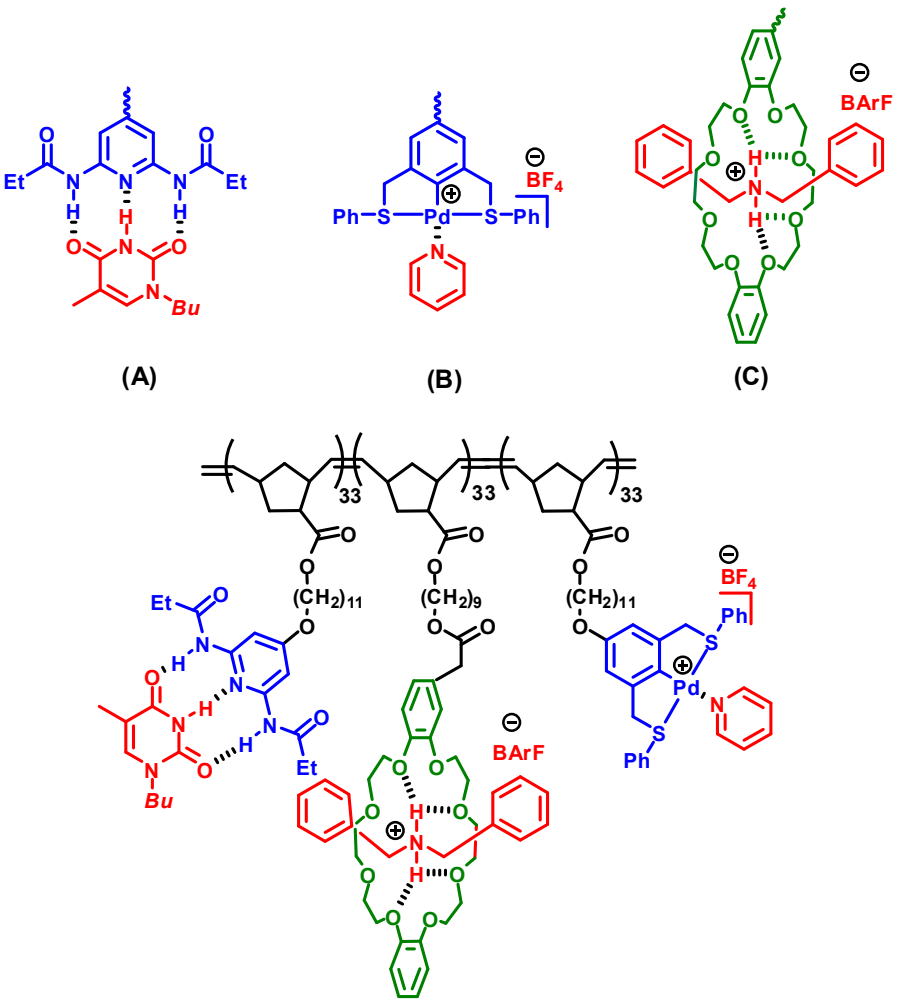


Figure 1.8 Three recognition motifs based on (A) hydrogen bonding interactions between 2,6-diaminopyridine and thymine, (B) metal coordination of SCS Pd pincer with pyridine and (C) pseudorotaxane formation between dibenzo[24]crown-8 (DB24C8) and dibenzylammonium ions, and (D) the fully functionalized **terpolymer-5**.

1.12 Applications of noncovalently functionalized side-chain copolymers

After having discussed self-assembly strategies towards noncovalently functionalized side-chain supramolecular polymers as well as studies on the orthogonality of using multiple noncovalent interactions in the same system, it is worthy to mention the potential applications of noncovalent side-chain polymer functionalization. In general this non covalent functionalization strategy can be used in two distinct areas, (i) for

polymer/materials functionalization in which the appropriately functionalized polymer scaffold is noncovalently functionalized with the functional moiety bestowing the desired function to the material[62,9,63] and (ii) for noncovalent crosslinking of the polymers to yield crosslinked networks which would show reversibility and stimuli responsive materials.

In Chapter two, the progress of using noncovalent interactions to reversibly crosslink polymer scaffolds to yield reversible and responsive materials will be discussed in detail. The chapter illustrates the importance of crosslinking technology in the field of materials science and the different approaches scientists have taken to overcome the significant drawbacks of conventional covalent polymer crosslinking. The chapter highlights the alternative reversible crosslinking processes based on different chemistries, but mainly focuses the advantages and the vast yet untapped potential of using noncovalent interactions based on molecular recognition to reversibly crosslink polymers yielding novel smart responsive materials. Such materials may address the requirements of emerging advanced applications.

Chapter three will discuss the synthesis of multi-functionalized block copolymers functionalized using metal coordination and hydrogen bonding interactions, it will be seen that by the combination of using a functionally tolerant "controlled" polymerization technique such as ROMP, with multiple noncovalent interactions highly defined polymeric structures with high functionality can be synthesized. Furthermore, such multi-functionalized polymer scaffolds can act as "Universal Polymer Backbones". Using this strategy, a parent 'Universal Polymer Backbone" can give rise to a family of daughter polymers upon using the appropriate noncovalent side-chain functionalization. To utilize

this strategy it is imperative, that the multiple noncovalent interactions must be orthogonal or at least the effect of one noncovalent interaction over the other must be quantitatively studied. Chapter three will focus on the orthogonality between hydrogen bonding and metal coordination interactions; furthermore it shall discuss the dependence of the stability of the hydrogen bonding complex formation on important factors such as polymer molecular weight and block copolymer composition.

Chapter four will discuss multi-functionalization of a random copolymer using simultaneous hydrogen bonding interactions and ionic charge interactions. Chapter four will discuss ROMP to polymerize ionically charged monomers to yield charged polymers. Furthermore, ROMP will be utilized to copolymerize the charged ionic monomer with hydrogen bonded functionalized monomer, to form random multi-functionalized side-chain polymers which have both ionic charges and hydrogen bonding moieties. The orthogonality between the hydrogen bonding and ionic charge interactions will then be studied in detail, by using qualitative as well as quantitative analyses. Again, it will be shown that these multi-functionalized polymer scaffolds can be seen as "Universal Polymer Backbones". These 'Universal Polymer Backbone" upon side-chain functionalization can give rise to a family of varied daughter polymers stemming from a single parent polymer backbone.

For the application of multi-functional methodology for reversible polymer crosslinking, Chapter five will discuss in detail on the synthesis and characterization of complementary hydrogen bonded networks. Chapter five will mainly illustrate the hydrogen bonded networks obtained by reversibly crosslinking cyanuric functionalized polymers. This chapter will focus on the specific advantages of using complementary

hydrogen bonding interactions over self-dimerizing interactions to obtain hydrogen bonded crosslinked materials. Furthermore, the chapter will focus on the importance of the role of the crosslinking agent in modulating the network microstrucutre and hence the final materials properties of the crosslinked networks.

In Chapter six, the importance of the molecular structure of the hydrogen bonding motif used for inter-chain crosslinking in complementary hydrogen bonded networks will be discussed. The chapter will focus on hydrogen bonded crosslinked networks synthesized from polymers functionalized with thymine side-chains. The network properties of analogous thymine and cyanuric acid polymer networks will be compared and discussed focusing on the difference in the structure of the hydrogen bonding motif used for inter-chain crosslinking in the two systems.

Chapters five and six focus mainly on one type of hydrogen bonding motif used for synthesizing hydrogen bonded crosslinked networks. Chapter seven will focus on multi-functional complementary hydrogen bonding interactions based on cyanuric acid and thymine functional groups for inter-chain crosslinking. It will be seen that by combining multiple complementary hydrogen bonding motifs with vastly different association constants, it is possible to modulate and control the network microstructure at room temperature without the need for any thermal gradients, which are usually required for conventional hydrogen bonded systems. Furthermore, by employing crosslinking agents with different functional groups, the polymer networks can be either de-crosslinked or re-crosslinked yield materials which have significantly differing mechanical properties.

The application and specific advantages of complementary hydrogen bonded polymer networks were discussed in detail in Chapters five-seven. Chapter eight will briefly focus on metal coordinated crosslinked networks based on SCS Pd pincer centers and pyridine complexes. The importance of using metal coordination interactions for reversible polymer crosslinking will be addressed. Furthermore, the network properties of the metal crosslinked system will be compared with those of the hydrogen bonded crosslinked networks.

In Chapters' five to eight, the application of only one type of noncovalent interaction, either hydrogen bonding or metal coordination for reversibly crosslinking polymers was discussed. Chapter nine will discuss the synthesis and characterization of multi-functionalized multi-responsive networks in which both hydrogen bonding and metal coordination interactions will be used to crosslink a multi-functionalized polymer scaffold. Chapter nine will discuss the application of the "Universal Polymer Backbone" concept discussed in Chapter two. It will illustrate how one can combine two different orthogonal noncovalent interactions to transform a single polymer backbone into materials having vastly different mechanical properties and responsiveness.

Chapter ten will discuss the future outlook and potential applications for side-chain multi-functionalized systems. This chapter will focus on the vast potentials of applying the concept of multi-functionalization of side-chain polymers in the field of materials science.

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CHAPTER TWO

Application of Side-Chain Supramolecular Copolymers: Reversible Stimuli Responsive Crosslinked Polymer Networks

2.1 Introduction

The process of transforming a linear polymer structure into a three-dimensional network structure in which the individual polymer chains are linked together is known as polymer crosslinking. The discovery of polymer crosslinking is one of most important events in the development of materials and polymer science. However conventional polymer crosslinking has been completely based on covalent chemistries.

Although highly successful covalent crosslinking is essentially a unidirectional crosslinking approach and has its serious disadvantages. One of the most serious problems of irreversibly crosslinked polymers is the inability of the material to be recycled efficiently. With the growing use of polymers as in the case of commodity thermoset polymers, environmental pertinent issues such as recycling of plastics are important considerations. Crosslinked polymers are difficult to process and recycle an important goal in today's society. While it must be noted that the development of crosslinking technology was spurred due to the need for superior materials properties, the current research in materials science mandates more stringent demands, such as self-reparability, highly controlled and functionalized materials, stimuli responsive materials for applications ranging from photo-lithography, catalysis, biodegradable materials, to enhanced biomedical scaffold materials to drug release agents. Stimuli-responsive materials are needed for advanced technologies for the control of fluidity, viscoelasticity, solvent volatility, and material transport.

Despite the disadvantages of conventional covalent crosslinking, the vast numbers of crosslinked polymers are still based on covalent crosslinking techniques. However, the growing needs of technological innovation cannot be met by utilizing covalent chemistry. Thus there exists a vast opportunity for other unconventional crosslinking techniques based on noncovalent chemistry to carry the advancement in material science to the next level. This chapter critically evaluates the attempts made by various scientists to use novel techniques to crosslink polymers to yield materials which not only display the usual superior materials characteristics, but also display increasing relevant attributes such as reversibility and responsiveness.

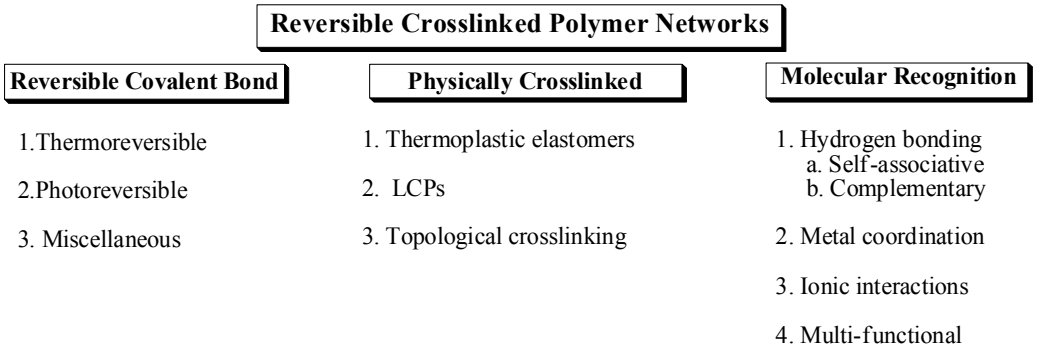


Figure 2.1 Schematic description of the major classification of reversibly crosslinked polymer networks.

2.2 Reversible crosslinking of polymers using covalent bonds

Polymers which can be crosslinked by using labile covalent bonds can be classified into two main systems as shown in Figure 2.1, thermally-labile bonds, photoreversible bonds. Dynamic covalent chemistry relates to chemical reactions carried out reversibly under conditions of equilibrium control, such a system can offer the possibility of "doing supramolecular chemistry" at the level of covalent bonds.[1] If a polymer consists of dynamic covalent bonds, it can behave as a reorganizable polymer similar to noncovalent systems. However, in contrast to noncovalent systems, polymers with dynamic covalent bonds are stable under ambient conditions and even under high dilution concentration conditions. Nevertheless, once they are exposed to external stimuli such as heating, they can be reorganized to the proper form that reflects the chemical and physical environmental conditions.

The employment of dynamic covalent bonds which would quantitatively dissociate or cleave under a suitable agent such as temperature or UV radiation can be used for the synthesis of reversibly covalently crosslinked polymers. Such a dynamic covalent bond must however not be too stable since this result in inefficient decrosslinking and would require very stringent conditions, which would result in several

side-reactions such as chain-degradation and oxidation. For practical considerations, the reversible crosslinking/decrosslinking reaction conditions must be mild enough so as not to degrade the polymer main-chain, cause side-reaction such as free radical formation. Furthermore, the reaction must have a sufficiently high yield and must be sufficiently fast so as to allow practical applications. The obvious benefits of using such as systems is that we can successfully combine the superior properties of crosslinked polymer networks as well as retain the benefits of converting the crosslinked material to a linear "thermoplastic" material.

2.2.1 *Thermally reversible polymer networks*

Thermally reversible covalent (TRC) crosslinked polymers are covalently crosslinked polymers, which undergo decrosslinking at elevated temperatures. In such systems the covalent inter-chain crosslinks are thermally labile and hence exhibit thermoplasticity at higher temperatures. However the reversible reaction must most involve the loss of byproducts, furthermore both the forward and backward reactions must be temperature dependent and the covalent bond formation must take place at lower temperatures.[2] Such systems are hence expected to be similar to thermosetting polymers in their physical properties and solvent resistance in their crosslinked state but can be remolded by thermal processing technology as in the case of conventional "thermoplastic" uncrosslinked materials. Consequently, TRC crosslinking technology can be used for manufacturing recyclable materials and improving the mechanical properties of traditional thermoplastic materials. Additionally, linear polymers with TRC linkages in their backbone are expected to exhibit lower viscosities on heating than typical linear polymers and to be processed at lower shear rates. Several approaches have been utilized

to obtain TRC materials however the most successful system has been based on Diels-Alder based systems.

2.2.1.1 *Diels-Alder reaction crosslinked polymers*

The Diels-Alder reaction provides a simple, efficient, and clean route to generate carbon based bonds by inter- or intra-molecular coupling and represents one of the most widely used route to generate TRC materials (Figure 2.2).[3-11] It is a [4 + 2] cyclo-addition reaction, in which a dienophile (electron poor) adds typically to a conjugated diene (electron rich) to give a cyclic product called an adduct.

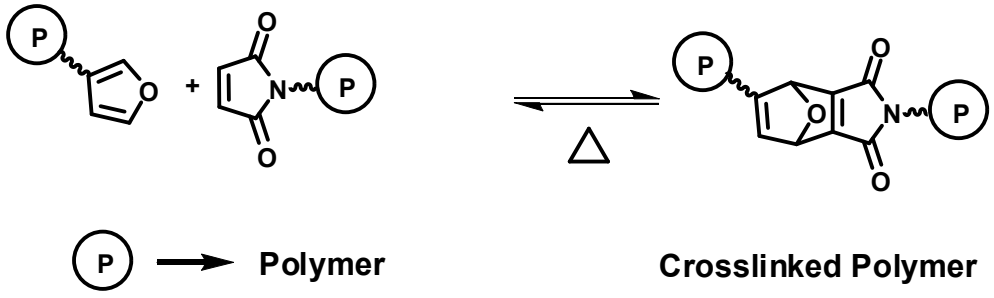


Figure 2.2 Example of Diels-Alder crosslinking of furan and maleimide functionalized polymers for reversible polymer crosslinking.

For polymer crosslinking, the dienes and dienophiles groups are either present as side-chain functional groups (as in side-chain functionalized polymers) or as main-chain polymers.[8] Alternatively reversible Diels–Alder cycloadditive dimerization of cyclopentadiene (CPD) or its derivatives has also been used for reversible polymer crosslinking. Since the Diels-Alder reaction is thermally reversible; its equilibrium can be easily displaced toward the starting compounds by heating (retro-Diels-Alder). The versatility of this reaction has allowed polymers belonging to a vast class of polymers

ranging from acrylates, to poly(amide)s, poly(ester)s, poly(siloxane)s, etc to be reversibly crosslinked. Gandini and coworkers used Diels-Alder reaction to synthesize new, thermally reversible, elastomeric networks. They synthesized a low T_g furan functionalized poly(hexyl acrylate) which was then reversibly crosslinked through the furan pendant group via a Diels-Alder reaction using a maleimide crosslinking agent to yield a gel like elastomeric material. This material could also be reversibly de-crosslinked by thermal treatment in the presence of an appropriate trapping agent via retro-Diels-Alder reaction which gave the original uncrosslinked polymer structure.[6] The use of Diels-Alder reaction for polymer crosslinking is for primarily the synthesis of thermally sensitive materials; however it has also been used for advanced applications. Jen and coworkers used a dendronized polymer functionalized with protected furan groups which was later reversibly crosslinked using Diels-Alder reaction by maleimide crosslinking agents. Such a TRC material was found to be a superior NLO material which also had a very high thermal stability.[11] Furthermore Hawker and coworkers have also used this approach to make materials for applications such as data-storage and lithographic applications.[7]

Even though we have seen the success of using Diels-Alder reaction for thermo-reversible crosslinking, it must be pointed out that the system has its own limitations. There have been reports which detail the instability of the functionalized polymers which undergo irreversible crosslinking through non-cyclization paths, furthermore the heat treatment required for complete decrosslinking also offers an important limitation for its practical applications.[3] Schiraldi and coworkers also used this approach to reversibly crosslink anthracene functionalized poly(ethyleneterephthalate) (PET) using maleimides.

Although they observed that they could successfully crosslink the polymers, the decrosslinking step was slow, inefficient and the process resulted in thermal degradation of the PET copolymer.[8]

2.2.2 *Photo-reversible polymer networks*

The second class of covalently crosslinkable materials use photo-reversible covalent bonds for the inter-chain crosslinking. Aromatic functional groups such as coumarin, cinnamate, and maleimides undergo 2 + 2 cycloadditions when exposed to UV irradiation and form crosslinking points via nonradical radiative pathways, negating the need for photoinitiators. Such photolabile covalent bond formation can be utilized for reversible polymer crosslinking reactions to yield materials which would be responsive to UV radiations. Derivatives of 7-hydroxycoumarin (Figure 2.3) photodimerize when irradiated in the ultraviolet-A (UVA) region of the electromagnetic spectrum (>300 nm).[12] The dimer, which is composed of a cyclobutane ring, can undergo cycloreversibility when irradiated at wavelengths shorter than 290 nm. One important advantage of photocrosslinking via the cycloaddition is that this reaction does not suffer from oxygen inhibition. Saegusa and co-workers synthesized polyoxazoline having a coumarin moiety as a pendent group and first demonstrated the photoreversibility of crosslinks using coumarin groups.[13]

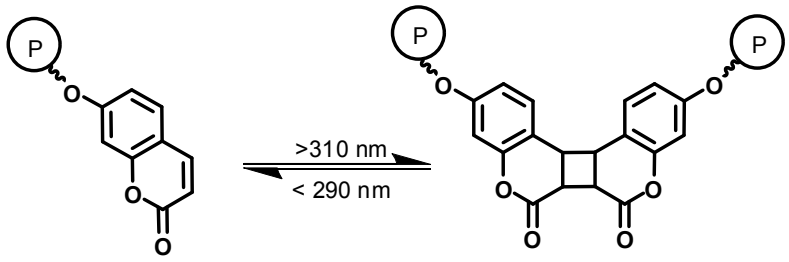


Figure 2.3 Photoreversible polymer crosslinking based on the photoreversible dimerization of 7-hydroxycoumarin.

Coumarin as a photo-cross-linkable group has several advantages such as high photosensitivity, particularly an efficient photoreversibility as well as biodegradability. Nagata and co-workers used photoreversible poly(ethylene glycol)s functionalized with pendant coumarin groups to form PEG hydrogels which underwent rapid reversible photocrosslinking , the degree of swelling could be controlled by the irradiation time and molecular weight of PEG. The facile photoreversibility of these hydrogels are of interest as substrates for drug delivery and biomedical applications.[14]

Zhao and coworkers have designed and synthesized a novel coumarin-containing amphiphilic diblock copolymer, which can form photocontrollable polymer micelles can be reversibly photo crosslinked and photo decrosslinked. Such a system allows for the increase stability of these polymer micellar aggregates (and their encapsulation) through photo-cross-linking and then to allow the release of encapsulated guest through photo-de-cross-linking-induced disruption of the micelles.[15]

2.3 Reversible crosslinking via physical crosslinking

In this group of materials, the polymer chains are linked together physically by exploiting the morphological variations in the different segments of the polymer.[16] The polymer chains not connected via covalent bonds, but due to the difference in the inherent molecular architecture of the polymer chains, the material exhibits a two (or more) phase system in which major phase is impregnated with localized domains of the minor phase. Generally the minor phase (hard phase) has a higher glass-transition temperature than the major phase (soft phase), and hence it acts as physical crosslinking points thus providing the necessary reinforcement for important materials properties such

as elasticity and mechanical strength. Since the material is physically crosslinked and the presence of these different domains are affected by thermal conditions, hence the material would exhibit thermoplasticity above the glass transition temperature of the reinforcing domain thus facilitating processing and recycling. Hence in this approach the difference in the macro or bulk architecture due to the difference in the molecular architecture of the polymer is used for reversible crosslinking. Segmented tri-block copolymers and liquid crystalline materials are important examples in this group of materials.

2.3.1 *Thermoplastic elastomers*

Thermoplastic elastomers are perhaps the most important commercial examples of physically crosslinked materials.[17] Due to the thermally reversible nature of the physical crosslinks, these materials exhibit superior mechanical properties while retaining their thermoplasticity. Furthermore the ability to tailor the hard and the soft segments of these block copolymers have made them highly tailor-made materials whose mechanical properties can be precisely tuned via polymer chemistry.[16] The most important example of these materials which has historically replaced conventionally crosslinked rubber is the SBS (styrene-butadiene-styrene) triblock copolymers.

2.3.2 *Liquid crystalline (LC) materials*

Liquid crystalline polymers have attracted much attention as a candidate for promising polymeric materials with high performance and high function.[18-23] LC polymers can be classified as main-chain and side-chain, which have mesogenic units in the main chain and side chains, respectively. For polymeric materials with high modulus and high strength at break, the main chain type LC polymer having a linear polymer backbone has been focused. Thermoplastic main chain polymers such as poly(ester)s,

poly(carbonate)s, poly(esteramide)s, and poly(urethane)s have been studied extensively. In the industry, these polymers are generally utilized as engineering plastics, but they possess processing problems because of their high melting temperature (T_m) and high melt viscosity, and so on. In order to improve their processability, several investigations have been carried out; for example, the incorporation of flexible segments into the main chain decreased the Tm of polymers. Combining LC segments with flexible segments is expected to form new materials with unique properties arising from the characteristics of two segments.

2.3.3 *Mechanically (topologically) interlocked systems*

In all the examples of polymer networks so far discussed the crosslinks were introduced by physical or chemical bonding and the concentration fluctuations or spatial inhomogeneities in polymer gels are topologically frozen by nature due to the presence of permanent networks. A relatively new class of gel materials is called “topological network” or ‘‘slide-ring gel’’, and is characterized by the sliding character of the cross-link points (also called slide-ring cross-link points).

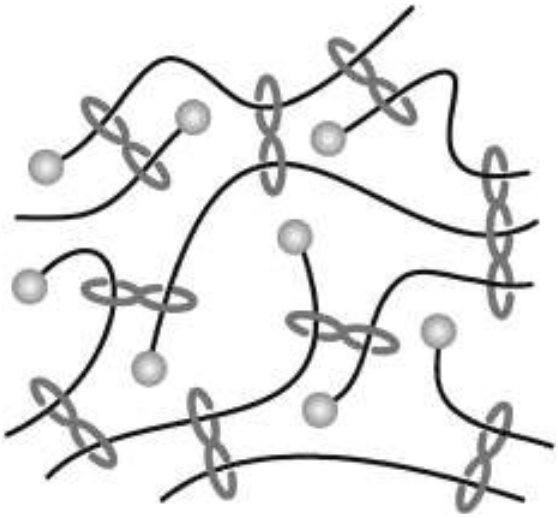


Figure 2.4 A schematic representation of a generic slide-ring gel.[24]

An essential difference between the slide-ring gels and conventional polymer gels is the presence of movable crosslinks, which allows a sliding motion of the constitutive template network chains through the Figure-of-eight junctions.[24] As shown in the Figure 2.4, a crosslink of slide-ring gel can move freely along the polymer chain to equalize the tension of the polymer chains just like a pulley. The sliding gels demonstrate unusual chemical, physical, and mechanical properties due to the theoretical ability of the crosslinking points to slide along the template polymer chain. It is expected that nanoscopic spatial inhomogeneities and local stresses may be automatically relaxed by a sliding motion of the movable crosslinks. These movable cross-links allow high extensibility, large degree of swelling, and large reversible-deformability. This specific crosslinking structure of slide-ring gel shows different mechanical properties in contrast to conventional chemical gels and rubbers.

2.4 Reversible crosslinking using molecular recognition processes

The third class of reversibly crosslinked polymer networks is based on noncovalent interactions. Noncovalent crosslinking of polymers using molecular recognition processes such as hydrogen bonding, metal coordination, and Coulombic interactions have been employed to reversibly crosslink side-chain functionalized copolymers. Such an approach offers the advantage that it can be used to crosslink reversibly polymer chains without chain degradation or other side-reactions. By utilizing a suitable molecular recognition process with a sufficiently large equilibrium constant quantitative reversible crosslinking can be achieved without any side-reactions or chain

degradation. Besides the inherent advantages of noncovalent crosslinks such as reversibility and a greater control over the network architecture, noncovalent strategies also allow for the tuning of materials properties due to the responsiveness of these interactions and ultimately the material towards external stimuli. For example, the employment of metal coordination for noncovalent cross-linking results in materials those are sensitive towards redox reactions or metal-ligand displacement agents, whereas the use of hydrogen bonding interactions yields thermally sensitive materials. Clearly, noncovalent crosslinking strategies offer a route towards responsive materials with tunable properties that are otherwise not accessible.

2.4.1 *Network formation using hydrogen bonding*

Hydrogen bonding is among the most widely used noncovalent interactions for the synthesis of reversible crosslinked polymeric networks. The advantages of using hydrogen bonding interactions for reversible crosslinking are that the crosslinks are thermally reversible and further the strength of hydrogen bonded complexes (and hence the crosslinking strength) can be tuned easily by (i) varying the number of hydrogen bonds in a receptor system from single, dual, triple, quadruple to sextuple or even higher order hydrogen bonding motifs, (ii) changing solvent or temperature or (iii) altering the acidity and/or basicity of the donor (D) and acceptor (A) moieties.

In polymer melts, even weak hydrogen bonded complexes can be used for polymer crosslinking when combined with additional stabilization factors. Rowan and coworkers have used telechelic polymers based on adenines and cytosines which form weakly bonded hydrogen bonded complexes (association constant $< 5\ M^{-1}$). They found that combination of weak hydrogen bonding with phase separation resulted in thermally

sensitive crosslinked polymer melts. Polymeric networks based on hydrogen bonding can broadly be classified into two classes distinguished by the origin of crosslinks due to a) self-association or b) addition of an external "crosslinking agent".

2.4.1.1 *Self-associative polymer networks*

In self-associative polymer networks (often called one component systems), the hydrogen bonding recognition units that are covalently attached to the polymer backbone have an appreciable tendency for self-association, i.e. self-dimerize, which leads to inter-chain crosslinking of the polymers. As a result, the system is inherently crosslinked and does not require any external crosslinking agents for network formation (Figure 2.5).

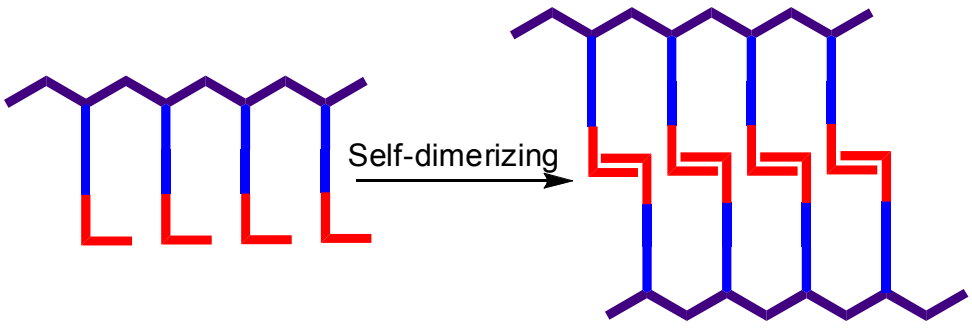


Figure 2.5 Hydrogen bonded crosslinked polymer based on self-dimerizing hydrogen bonding recognition units.

Since the crosslinking is based on dimerization phenomena, to achieve effective crosslinking the functional groups attached to the polymer chains must exhibit very high dimerization tendency, i.e. they have to have high dimerization constant. If weak interactions are employed, additional stabilizing effects such as phase separation are needed to form crosslinked three-dimensional networks. Self-associative polymer networks based on the dimerization of urazole units (two-point hydrogen bonding)[25], 2-ureido-4[1H]-pyrimidone (four-point hydrogen bonding)[26], simple carboxylic acid groups (two-point hydrogen bonding)[27], sulfonamide (two-point hydrogen bonding), and 1, 2, 4-triazole[27] (three-point hydrogen bonding) have been reported (Figure 2.6).

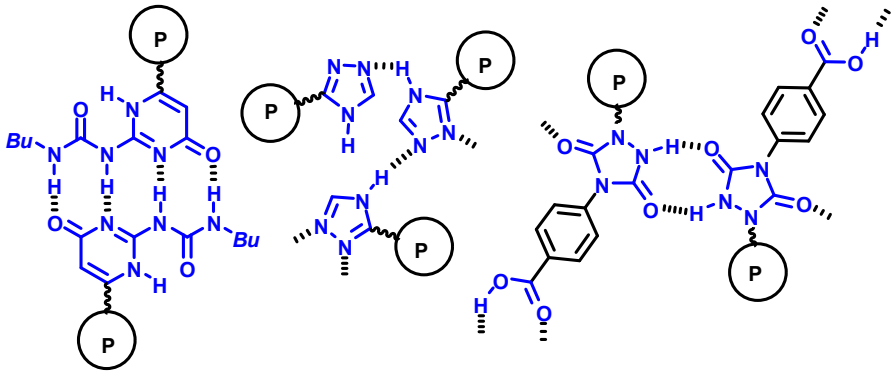


Figure 2.6 Self-associative hydrogen bonded polymer networks based on (A) 2-ureido-4[1H]-pyrimidone (UPy), (B) 1,2,4-triazine, and (C) urazole carboxylic acid.

Examples of self-associative polymer networks using hydrogen bonding include the work by Stadler and co-workers who reported reversible polymer network formation via intermolecular hydrogen bonding of (4-carboxyphenyl)urazole groups attached to the side-chains of poly(isobutylene).[28] Effective crosslinking results from the two-point hydrogen bonding dimerization of the urazole moieties as well as the carboxylic acid groups. While the individual two-point hydrogen bonding interactions are fairly weak

(K_{dimer} less than 100 M^{-1} in chloroform), the system also is based on highly ordered two-dimensional urazole clusters that phase separate from the amorphous non-polar polymer resulting in additional stabilization of the crosslinked polymeric network. Meijer and co-workers have reported the use 2-ureido-4[1H]-pyrimidone (UPy) (Figure 2.7), a hydrogen bonding array that dimerizes through an array of four hydrogen bonds in a self-complementary (DDAA) manner with a dimerization constant as high as 6 x 10^7 M^{-1} in chloroform, to crosslink polymers.[29] Similar approaches using UPy as cross-linking directing group have been reported by Long and coworkers who functionalized poly(methylmethacrylate) using UPy to form a self-associative polymer network.[26] Furthermore; Coates copolymerized UPy functionalized monomers with 1-hexene to form polyolefin-based elastomers.[30]

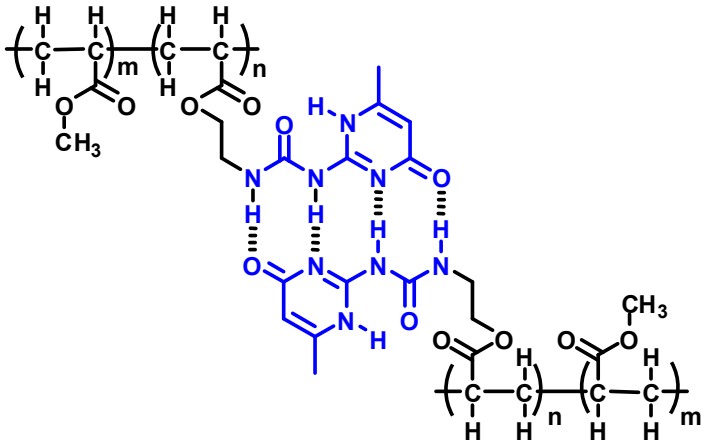
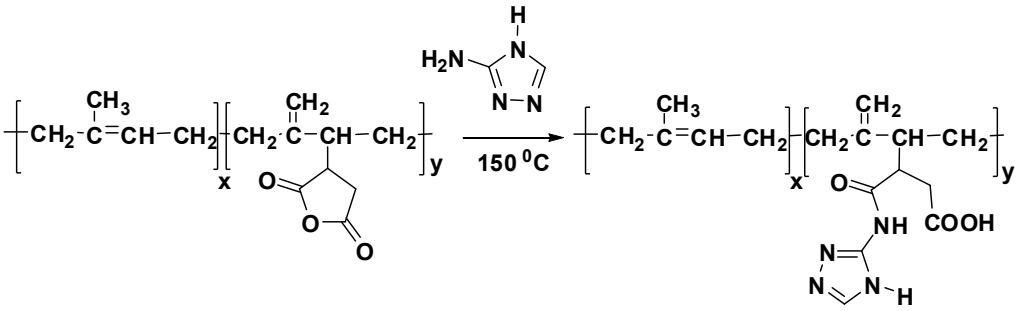


Figure 2.7 Self-associative polymer network formed via the dimerization of 2-ureido-4[1H]-pyrimidone groups attached to the polymer backbone.

Chino and coworkers functionalized maleated poly(isoprene) with amino triazole to form a functionalized polymer with pendant triazole and carboxylic acid groups. The

hydrogen bonding interactions between the functional groups resulted in hydrogen bonding units which resulted in the superior properties of the functionalized rubber.[27]



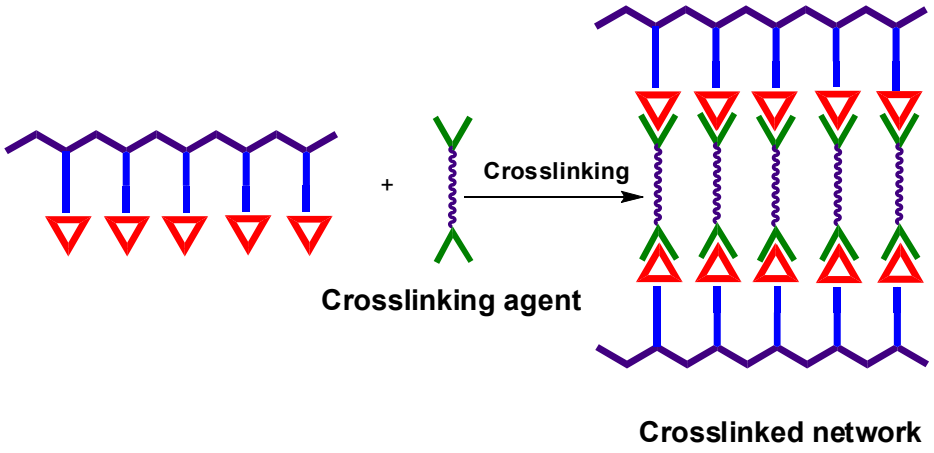
Scheme 2.1 Post-polymerization functionalization of maleated poly(isoprene) by triazole to form a self-associative network.

Although self-complementary polymer networks clearly show distinct advantages over conventional covalent crosslinked polymers, a limitation of this system is that the system always remains "crosslinked" and would exhibit "uncrosslinked" behavior only at temperatures above the hydrogen bond dissociation temperature. Since this system relies on the dimerization of the functional groups that are covalently attached to the polymer chains, the system displays some of the same limitations as covalent ones. As a result, to tune network properties such as the degree of crosslinking or the crosslinking density new generations of optimized polymeric material has to be redesigned and resynthesized. Therefore, this strategy does not allow for the full exploitation of the advantages of supramolecular self-assembly.

2.4.1.2 *Complementary hydrogen bonded polymer networks*

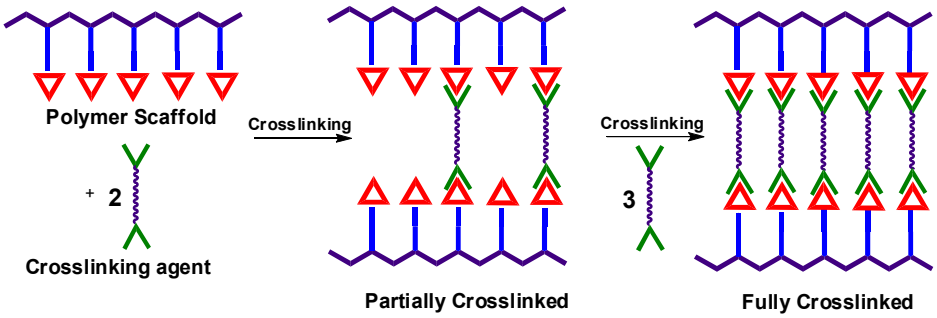
In polymeric networks that are based on the employment of complementary linkers - two component system - the hydrogen bonding recognition units attached to the polymer chains undergo little or no self-association and hence cannot effectively "crosslink" the polymer chains. Such a system represents an "open" system. An external

chemical agent or a "crosslinking agent" has to be added that is able to undergo hydrogen bonding with the recognition groups attached to the polymer side-chains resulting in the effective crosslinking of the polymer chains through inter-chain hydrogen bonding as depicted in Scheme 2.2.



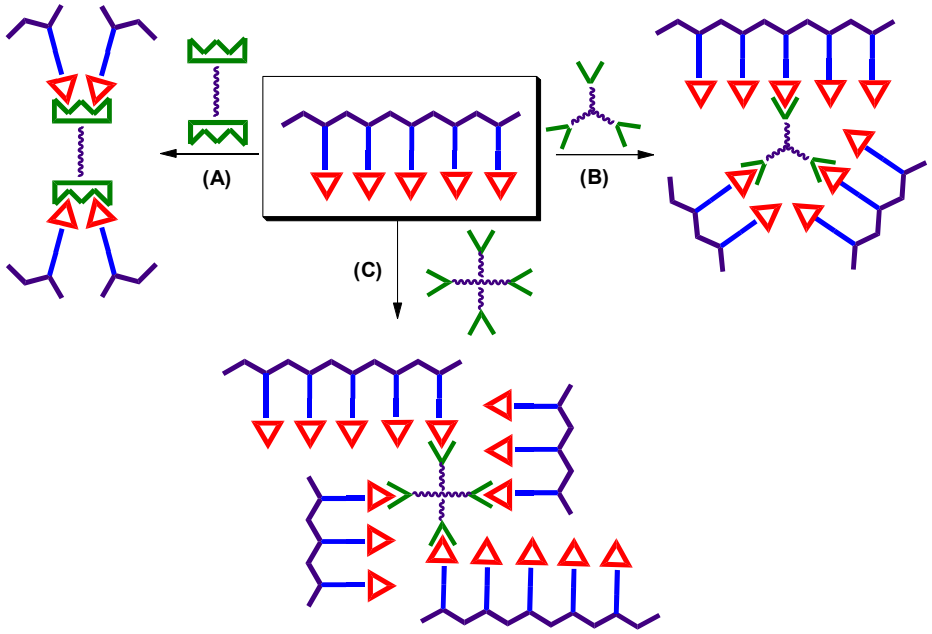
Scheme 2.2 Hydrogen bonded crosslinked polymer based on complementary hydrogen bonding recognition units.

In such a system, a polymer can be converted from being a completely "uncrosslinked" materials, i.e. no crosslinking agent present, to a completely "crosslinked system" with the addition of exactly one equivalent of crosslinking agent based on the recognition motifs along the polymer backbone.



Scheme 2.3 Hydrogen bonded crosslinked polymer based on complementary hydrogen bonding recognition units.

Changes of the stoichiometry of the recognition site/linker ratio can be used to tailor the physical properties of the resulting polymeric network and therefore obtain a range of materials ranging from highly viscous fluids to highly viscoelastic solids all resulting from the same parent polymer depicted in Scheme 2.3.



Scheme 2.4 Schematic representation of different polymer network formation based on the addition of complementary linkers from the same polymer scaffold using (A) bifunctional crosslinking agent based on six-point hydrogen bonding interaction, (B) trifunctional crosslinking agent based on single-point hydrogen bonding interaction and (C) tetrafunctional crosslinking agent based on single-point hydrogen bonding interaction.

The network strength of these systems also can be altered by varying the stability of the hydrogen bonded complex formation between the crosslinking agent and the

functional groups attached to the polymer chains. For example, the Weck group has demonstrated that networks based on three-point hydrogen bonding complex formation between 2,6-diaminopyridine and thymine ($K_a \sim 10^3$ M^{-1}) exhibit lower solution viscosities in chloroform as compared to similar systems in which the network is based on a stronger six-point complex formation between cyanuric acid and isophthalamide wedge receptors ($K_a \sim 10^6$ M^{-1}).[31] Another important factor in tuning the network properties is the molecular architecture of the crosslinking agent; by varying the functionality of the crosslinking one can control the crosslinking density of the network. As a result, the addition of one equivalent (based on recognition sites not linker to polymer ratio) of a tetrafunctional crosslinking agent will result in greater crosslinking efficiency as compared to the addition of two equivalents of a difunctional crosslinking agent. These advantages of the two component crosslinking systems allow for tunability of network properties when compared to the one component system described above. However, the number of reports in the literature using such a two-component system is limited when compared to the one component systems.

Kato and co-workers have crosslinked a supramolecular side-chain liquid crystalline polymer with side-chain carboxylic acid groups by using bis-imidazoyl or bis-pyridine compound as the crosslinking agent (Figure 2.8 A and B respectively). The addition of the bis-pyridine caused inter-chain crosslinking through the one-point hydrogen bonding of the side-chain carboxylic groups with the bis-pyridine resulting in crosslinking and increased mesophase stability of the liquid crystalline state.[32]

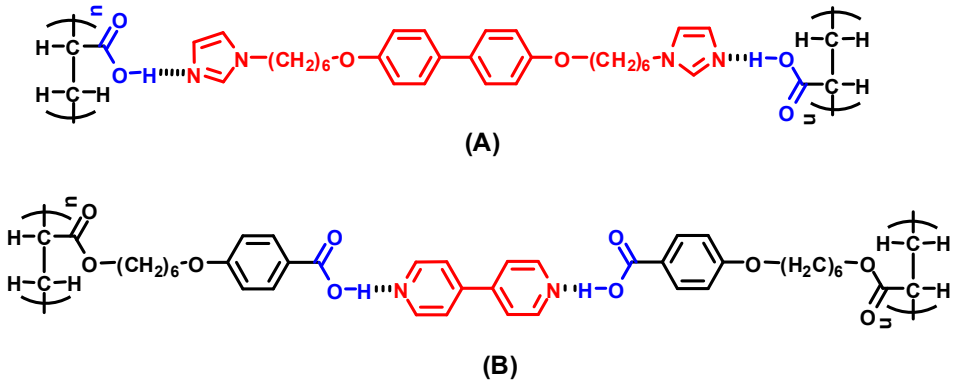


Figure 2.8 Examples of linker-crosslinked polymer networks exhibiting LCP characteristics.

As explained earlier, the role of the crosslinking agent is key in two component systems and affects the properties of the final network. The work of Rotello and co-workers illustrates the importance of the crosslinking agent. They employed bis-thymine based crosslinking agents with different linker lengths to reversibly crosslink 2,6-diaminopyridine functionalized copolymers (Figure 2.9) that formed discrete micron-sized spherical polymeric aggregates.[33] In their study, they demonstrated that the linker length influenced the median diameter of the spherical aggregate formed resulting in good control over the aggregate dimension.

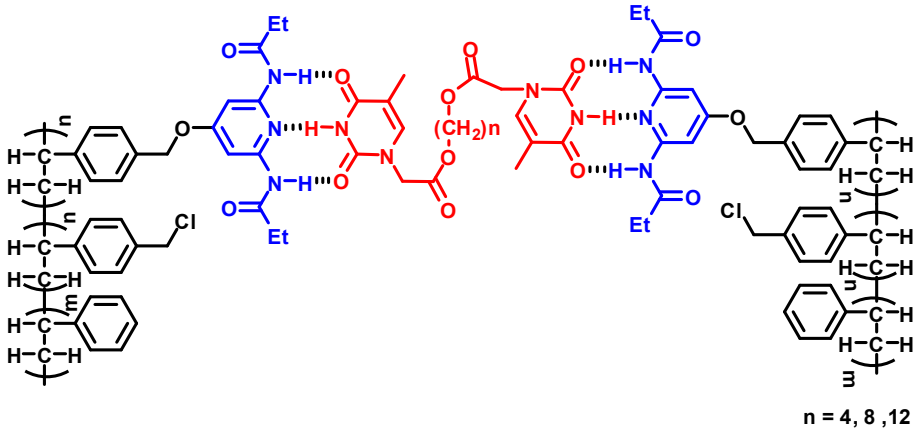


Figure 2.9 2,6-Diaminopyridine side-chain functionalized poly(styrene) crosslinked via bis-thymine crosslinking agents.

2.4.1.3 *Polymer networks based on polymer blends*

The physical combination of two or more chemically-different polymers to yield a hybrid material possessing the desirable properties of all the combined polymers has been a well-established part of materials science. However serious challenges such as the inherent immiscibility of different polymers leading to phase separated materials have to be overcome for materials applications. Many strategies have been used to minimize interfacial energy and to reduce the propensity for phase separation, including the use of compatibilizers, introduction of reactive groups to covalently connect individual polymers within the blend. One strategy to overcome microphase separation is the use of hydrogen bonding interactions. The polymers that need to be blended can be functionalized with complementary hydrogen bonding functional groups and, when blended either in solution or the melt, can undergo inter-chain hydrogen bonding interactions between the two inherently immiscible polymers thereby suppressing phase separation and forming a homogeneous polymer blend. Most systems described in the literature rely on fairly weak hydrogen bonding complexes based mainly on single or two-point interactions between functional groups such as hydroxyl, carboxyl, pyridyl, and amino groups. As a result of the weakness (low association strength) of the resulting complexes, to achieve homogenous blend formation high mole percentages of the hydrogen bonding functional groups are required. Unfortunately, this often results in materials with undesirable properties such as hygroscopiscities or high frictional coefficients. Zimmerman and co-workers have reported a system that ahs the potential to overcome these shortcomings. They employed a four-point hydrogen bonding system between urea of guanosine (UG) and 2,7-diamido-1,8-naphthyridine (DAN) which has an

association constant of $K_a \sim 5 \times 10^7$ M^{-1}, to blend two immiscible polymers such as poly(styrene) and poly(butylmethacrylate). They were able to demonstrate that a mixture of poly(styrene) and poly(butyl methacrylate) functionalized with DAN and UG respectively formed homogeneous blend (Figure 2.10) with no evidence of phase separation, even at a low concentration of the hydrogen bonding functional groups.[34]

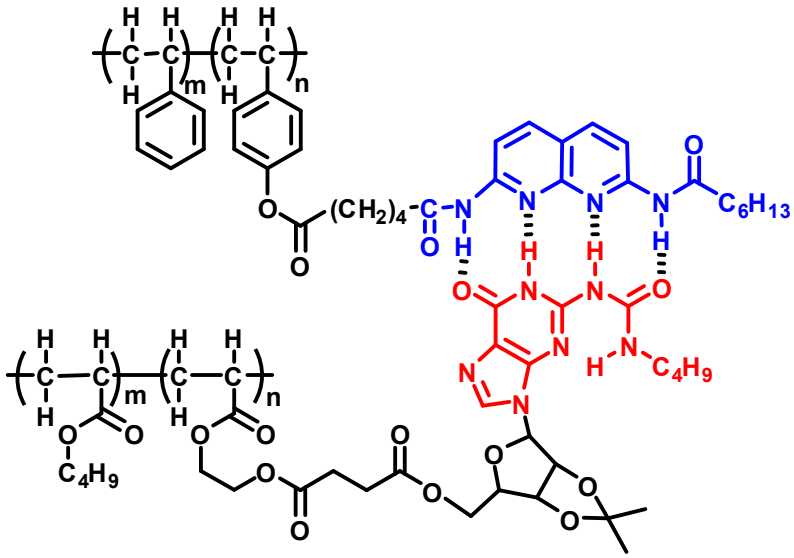
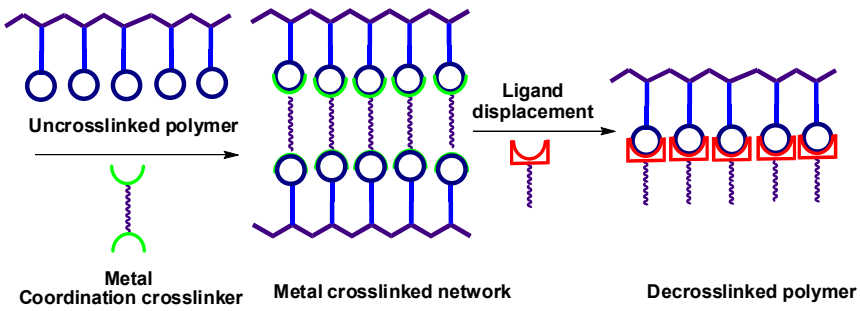


Figure 2.10 Homogenous polymer blend of DAN functionalized poly(styrene) and UG functionalized poly(butylmethacrylate) based on the four-point complementary complex formation between DAN and UG.

2.4.2 *Network formation using metal coordination*

The second class of noncovalent interactions that have been employed in polymer crosslinking is metal coordination. Metal coordination has a number of advantages to hydrogen bonding. First, metal coordination is among the strongest noncovalent interaction used in self-assembly in a variety of solvents (such as halogenated and aprotic ones) and the solid state. Second, while hydrogen bonding is generally thermo-reversible, metal-coordination is essentially chemo-reversible, i.e. crosslinking by metal-coordination can be reversed by a chemical species depicted in Scheme 2.5.[31]



Scheme 2.5 Cartoon representation of metal coordinated crosslinking of a functionalized polymer scaffold to yield chemoresponsive network.

Furthermore the introduction of metal centers into a crosslinked matrix also potentially confers distinct function to the material such as phosphorescence or fluorescence. Although not belonging to the class of side-chain functionalized polymers, Rowan and co-workers report a class of metallo-supramolecular gels which are multi-responsive and multi-stimuli as well as having the capability of photo-electroluminescent materials.

Crosslinked polymers based on metal coordination can be broadly classified into two classes. The first consists of systems in which the metal center is covalently attached to the polymer backbone essentially consisting of "macromolecular metallic centers" and crosslinking is achieved through bi- or multi-functional small molecule ligands. The second class consists of "macroligands" which are then crosslinked by the addition of bi-(or multi) functionalized metal complexes. Craig and co-workers have extensively studied metal crosslinked networks using poly(vinylpyridine) and bis-functionalized pincer complexes based on Pd and Pt (Figure 2.11 A). Since they employed a polymeric "macroligand" based on poly(vinylpyridine), they were able to noncovalently crosslink the same polymer chain by different bis-metal complexes, they used single as well as multiple metal complex formation for polymer crosslinking without any significant

interference of the different metal centers.[35] Similarly the Weck group has also used this metal coordination motif to crosslink their Pd metal containing polymers using bis-pyridine crosslinking agents (Figure 2.11 C).[31]

Schubert and co-workers have used terpyridine-based metal coordination for polymer crosslinking. They post-polymerized a commodity plastic such as poly(vinylchloride) to introduce terpyridine moieties in the side-chains. The functionalized polymer was then crosslinked by complexation of the terpyridine groups with ruthenium to form a metal crosslinked polymer (Figure 2.11 B). This example illustrates the importance of using "post-polymerization" functionalization in converting easily available commodity plastics into high value materials.[36] Furthermore, Schubert and co-workers have crosslinked a terpyridine functionalized poly(methacrylate) polymer using Fe (II) and Zn (II), and demonstrated that the addition of Fe(II) resulted in more efficient crosslinking than the addition of Zn(II). They also completely decrosslinked the Zn(II)-based network by the addition of HEEDTA [hydroethyl-(ethylenediaminetetriacetic acid)], thus demonstrating the complete reversibility of metal crosslinked polymers.[37]

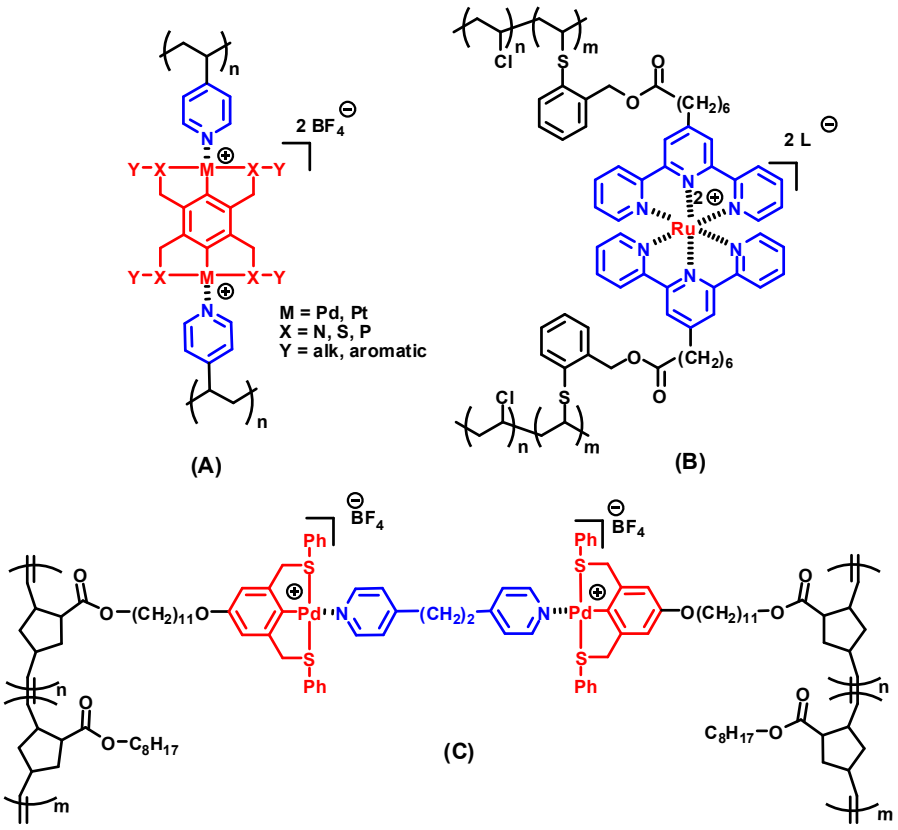
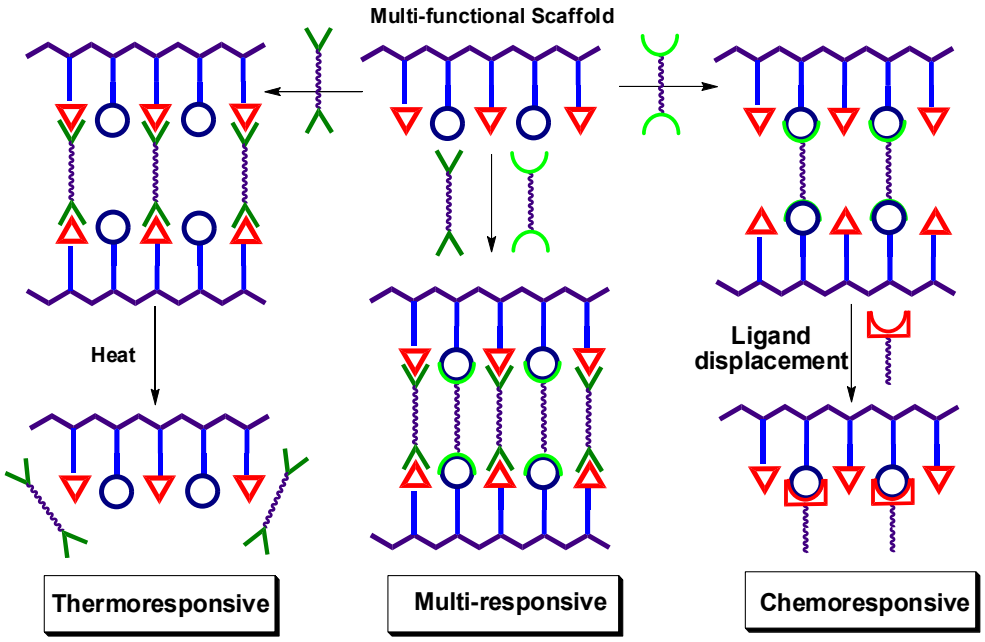


Figure 2.11 Examples of side-chain functionalized metal crosslinked polymer networks.

2.4.3 *Multi-functional polymer networks: Combining hydrogen bonding and metal coordination*

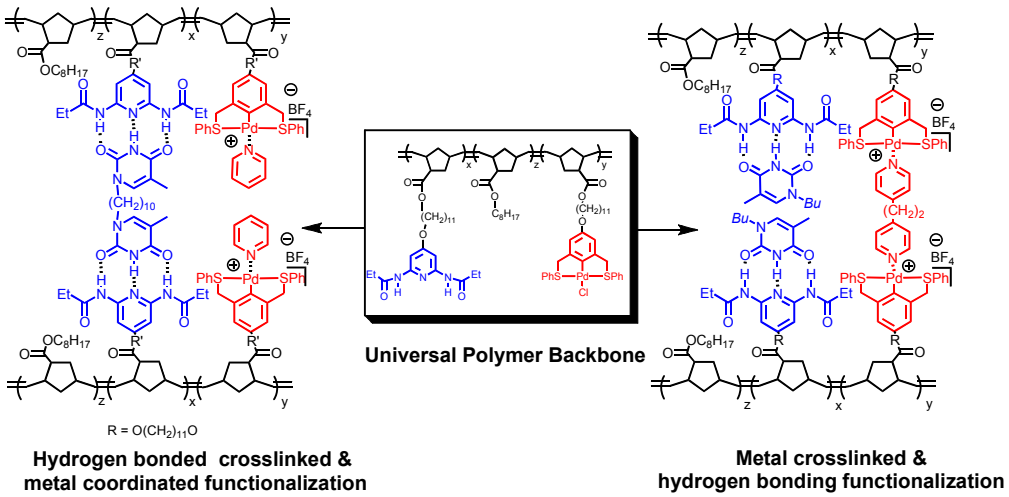
Side-chain functionalized polymers offer a strategy to use multiple noncovalent interactions that can be used to reversibly and simultaneously crosslink as well as functionalize the polymeric scaffolds to form highly functionalized crosslinked polymers with unprecedented complexity as illustrated in Scheme 2.6. This strategy involves the employment of an orthogonal functionalization and crosslinking strategy. The functionalization is achieved by using mono-functionalized moieties which are noncovalently anchored to the scaffold whereas crosslinking is achieved by using bi-functional crosslinking agents to cause inter-chain crosslinking.



Scheme 2.6 Cartoon representation of multi-functional crosslinking of a multi-functionalized polymer scaffold to yield thermoresponsive network (via Hydrogen bonding crosslinking), chemoresponsive network (via Metal coordination crosslinking) and multi-responsive network (via simultaneous crosslinking).

When orthogonal noncovalent interactions for crosslinking as well as for functionalization results are employed both processes should be mutually independent and non-interfering. The Weck group have synthesized highly functionalized noncovalently crosslinked polymers prepared from single "Universal Polymer Backbone" *via* directional self-assembly processes using a combination of metal coordination and hydrogen bonding.[31] They report a functionalization/crosslinking strategy where the polymeric scaffold can be noncovalently crosslinked employing one of the self-assembly motifs while the second one is used for the noncovalent functionalization. The Weck system is based on a terpolymer functionalized with 2,6-diaminopyridine as the hydrogen bonding receptor moieties, palladated SCS pincer complexes for metal coordination, and

a third inert spacer monomer to increase the polymer solubility and to dilute the recognition units (Scheme 2.7).



Scheme 2.7 Orthogonal noncovalent crosslinking as well as functionalization strategy of terpolymer using hydrogen bonding and metal coordination interactions.

Two distinct crosslinking/functionalization Schemes were investigated: (i) crosslinking via hydrogen bonding interaction employing either a bis-thymine or bis-perylene unit while the palladated SCS pincer centers were used for polymer functionalization by metal coordination or (ii) crosslinking *via* metal coordination using a bis-pyridine crosslinking agent while the 2,6-diaminopyridine along the polymer scaffold were functionalized with thymine derivatives. Extensive polymer crosslinking was observed in all cases as investigated by viscometry. However, the metal coordinated crosslinked scaffolds exhibited significantly higher viscosity than its hydrogen bonded analogue. The independent, non-interacting behaviors of these two modes of self-assembly allowed for the creation of a self-assembled, multi-functional, and crosslinked material in one self-assembly step. The reversibility of this system was also studied. The polymer scaffold could be fully de-functionalized and de-crosslinked by (1) heating to disrupt the hydrogen bonds (thus exhibiting thermoresponsiveness), and (2) addition of

PPh_3 to break the metal-pyridine complex via competitive ligand interaction (thus exhibiting chemoresponsiveness). Hence by the employment of different noncovalent interactions one can design a system that is responsive to multiple stimuli, opening the potential for the easy fabrication of "smart materials".

2.5 Conclusions and future outlook

In this chapter the development of polymer crosslinking technologies has been discussed; in particular the limitations of using conventional covalent chemistry for polymer crosslinking have been elucidated. The employment of reversible molecular recognition processes has allowed not only for the reversible crosslinking of polymers but has also allowed for the development of stimuli responsive materials. In particular the combination of orthogonal molecular recognition processes for noncovalent crosslinking for the generation of multi-responsive materials is potentially very suitable. Such multi-responsive materials will play an important role in the development of next-generation smart materials.

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CHAPTER THREE

Noncovalently Functionalized Block Copolymers Possessing Both Hydrogen Bonding and Metal Coordination Centers

3.1 Abstract

In this chapter, di-block copolymers containing both hydrogen bonding and metal coordination sites have been synthesized by ROMP and subsequently functionalized using noncovalent interactions. The resulting block copolymers can be viewed as "Universal Polymer Backbones", as a wide variety of polymers with varying functionalities can be prepared by altering the noncovalent functionalization strategy of the same polymer backbone. The effect of degree of polymerization, block copolymerization, block copolymer composition and metal coordination on the hydrogen bonding interaction has been investigated. In general, none of these variables has a profound effect on the strength of the hydrogen bonding interactions along the polymer backbones suggesting that the metal coordination and hydrogen bonding are orthogonal to each other in block copolymers. Finally, the effect of the noncovalent functionalization on the thermal properties of the polymers was investigated. It was found that, functionalization by both hydrogen bonding and metal coordination reduced the glass transition temperature and thermal stability of the polymers.

3.2 Introduction

The emerging area of functional materials for advanced applications will require both a high degree of functionalization as well as a high degree of control over the molecular architecture.[1] Examples include highly functionalized polymers for a wide variety of applications ranging from bio-medical materials such as polymers for drug delivery to electro-optical materials.[2] Other polymeric materials with a high degree of control over their molecular architecture are used in applications such as thermoplastic elastomers and nano-scale lithography.[3] One major class of materials that has the potential to fulfill both of these characteristics, namely functionalization and architectural control, are block copolymers.[4] Block copolymers have the unique advantage that their properties can be easily tailored through several variables such as the choice of comonomers and the individual block lengths. Despite these advantages, the synthetic complexity of densely functionalized block copolymers that combine multi-functionalization and controlled block copolymer architecture makes them extremely rare. To efficiently synthesize such materials one would need a highly controlled and functional group tolerant polymerization route, coupled with a fast and easy functionalization strategy. This chapter illustrates such a system by combining block copolymer formation using ROMP coupled with a noncovalent functionalization technique strategy using self-assembly. In the previous chapters the suitability of ROMP for this application was explained in detail, namely because ROMP is a highly functional group tolerant and can yield polymers with controlled architectures.[5-7] Prior to this study, ROMP has been used to synthesize highly functionalized di- and tri-block copolymers in a fast and efficient manner.[8-11] However, all of these examples are based on covalent

functionalization strategies. A strategy that has been suggested in the literature to overcome this limitation is the use of noncovalent chemistry for the functionalization step, i.e. the use of supramolecular polymer chemistry.[12,13]

In this chapter, substituted 2,6-diaminopyridines and their complimentary recognition units, substituted thymines, have been used as hydrogen bonding moieties as shown schematically in Figure 3.1.

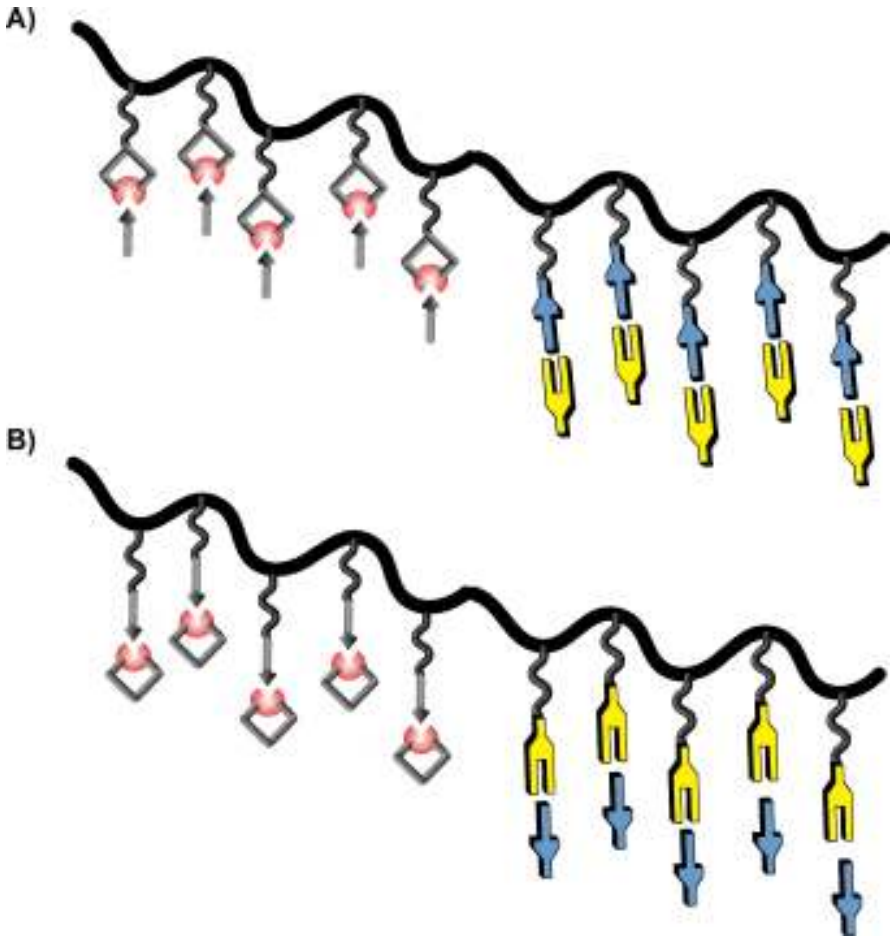


Figure 3.1 A cartoon depiction of block copolymers functionalized by complementary sets of recognition units based on hydrogen bonding and metal coordination. A) Block copolymer containing 'polymeric' metal complexes and B) block copolymer containing 'polymeric' ligands.

In the previous chapter it was discussed that metal coordination is the second class of noncovalent interactions that has been employed extensively in the literature.[18,19]

The main reasons for the use of metal coordination complexes in polymer science are their highly controlled synthesis, strong noncovalent bond strength, and the potential application of metal-containing polymers in areas such as supported catalysis,[35] light-emitting diodes[36] and chemically responsive gels.[14]

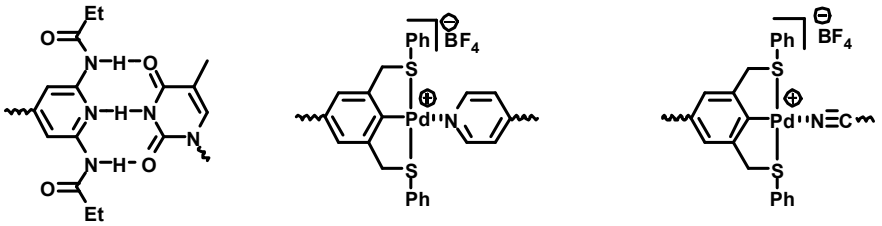
The combination of self-assembly with highly controlled polymerization techniques and complex polymeric architectures such as block copolymers has not been accomplished. Most literature reports employ random copolymers that have the advantage of being highly soluble and, in most cases, do not undergo phase separation. The employment of block copolymers in multi-step self-assembly is significantly more challenging due to these solubility and phase separation issues. This chapter reports the first example of the synthesis and subsequent fast and facile noncovalent functionalization of block copolymers having well-defined architectures by using multiple noncovalent interactions, i.e. hydrogen bonding and metal coordination motifs as noncovalent recognition sites. Such a strategy demonstrates the straight forward syntheses of highly functionalized polymeric materials with a high degree of control over their molecular architecture can be accomplished using self-assembly by combining functional group tolerant polymerization techniques, such as ROMP and noncovalent chemistry.

3.3 Design of monomers and recognition units

Multi-functional di-block copolymers having both hydrogen bonding and metal coordination sites are the basis of our research design. These polymers can be viewed as the development of the "Universal Polymer Backbones" concept as from a single polymer backbone a family of different functionalized polymeric materials can be

obtained by just varying the functionalization strategy by using self-assembly..[13] These polymer backbones are based on monomers that are comprised of three basic structural elements: a norbornene monomer that can be polymerized using ROMP, a long C-11 alkyl spacer to improve solubility and finally the recognition unit itself. During the course of this study, 100% isomerically pure *exo*-norbornene acid derivatives were used as precursors for the synthesis of all monomers. Isomerically pure *exo*-norbornenes have been shown to polymerize in a highly controlled fashion using the first generation Grubbs initiator making *exo*-norbornenes the monomers of choice.[43] Four recognition units have been covalently linked to the monomers that are either based on DAD-ADA three hydrogen bonding arrays or on palladium-based metal coordination motifs.

Three point hydrogen bonding DAD-ADA arrays are the most widely studied hydrogen bonding receptor systems to date.[44,45] In this work the DAD-ADA arrays are formed using two sets of functionalized 2,6-diaminopyridine (DAD) and thymine (ADA) complementary units as shown in Figure 3.2 A. The first set involves anchoring the 2,6-diaminopyridine recognition unit as the side-chain functionality onto the monomer with *N*-butyl thymine being the complementary recognition unit while the second set utilizes a thymine recognition unit covalently linked to the monomer with 2,6-diaminopyridine being used as the complementary recognition unit.



A **B-1** **B-2**

Figure 3.2 Self-assembly motifs employed in this study: A) Three point hydrogen-bonded complex between 2,6-diaminopyridines and thymine and B) metal coordination complexes of palladated SCS pincer system with pyridines (B-1) and nitriles (B-2).

In the previous chapters it was seen that, palladated sulfur-carbon-sulfur (SCS) pincer complexes are an important class of organometallic compounds which are widely used in catalysis[46,35] and functional materials.[47] In this study, the coordination of palladated SCS pincer systems with either nitriles or pyridines using again two sets of complementary units is utilized. The first set involves anchoring the palladated SCS pincer ligand as side-chain functionality onto the monomer with pyridine or functional nitriles as complementary ligands. The second set is based on a nitrile functionalized monomer that can be viewed, after polymerization, as a "polymeric" ligand. This polymeric ligand can then be functionalized by coordination of a palladated pincer center as the complementary coordination system. Figure 3.3 outlines the monomers and recognition units employed in this study.

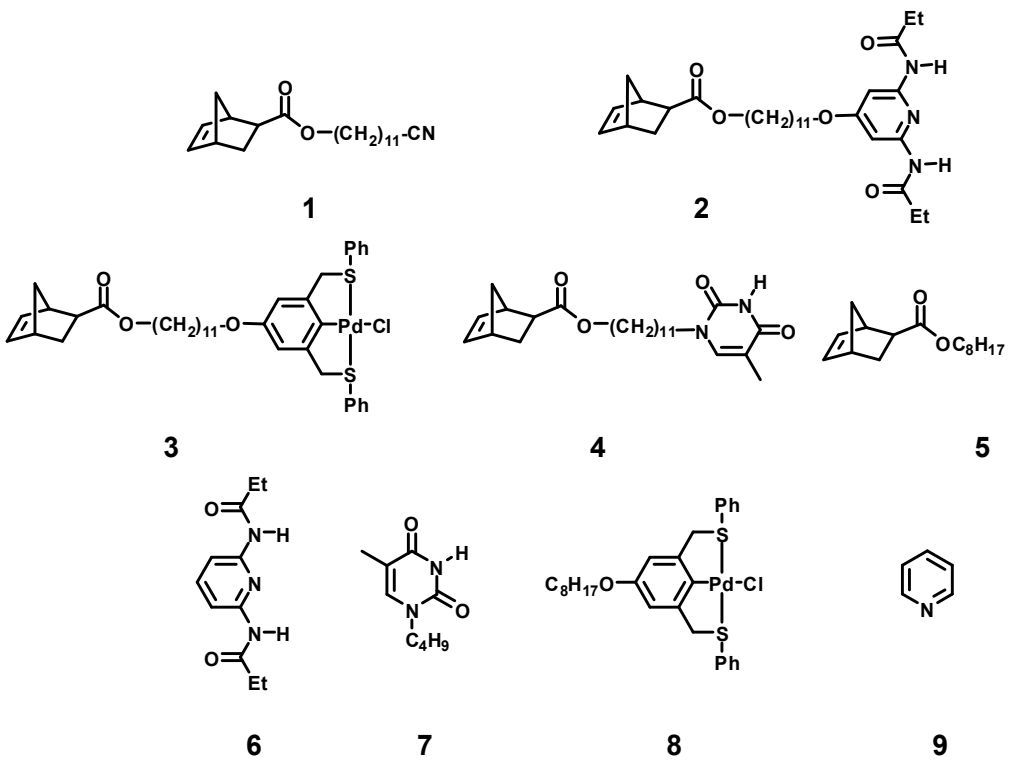
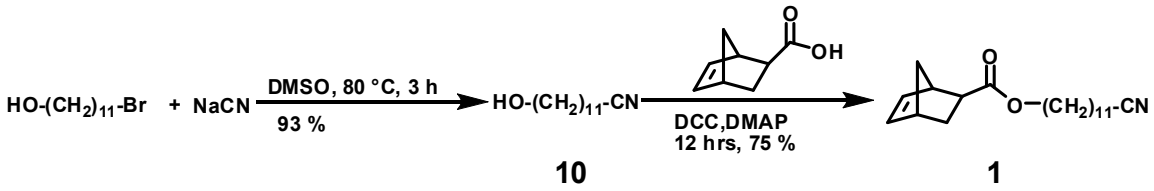


Figure 3.3 Monomers **1**-**5** and recognition units **6**-**9** utilized in this study.

3.4 Synthesis of monomers and recognition units

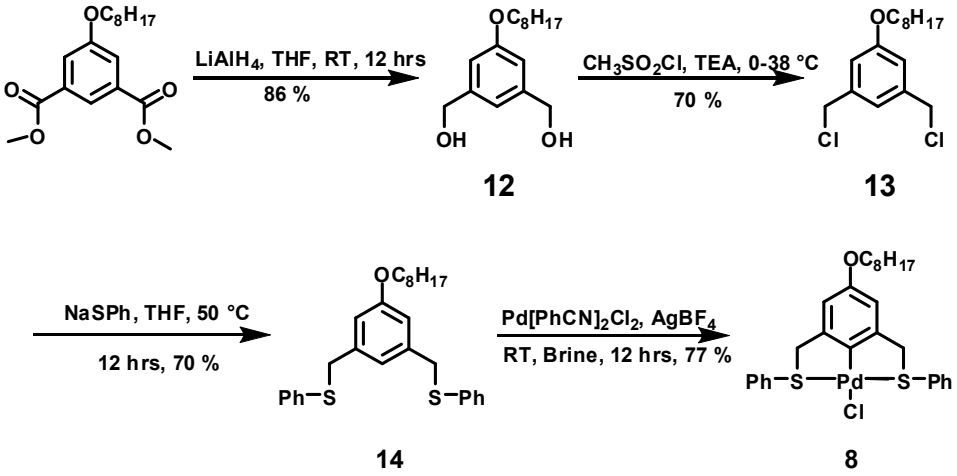
Monomer **1** was synthesized as outlined in Scheme 3.1 by converting 11-bromoundecan-1-ol to its corresponding nitrile derivative, **10**,[49] followed by esterification of **10** with the *exo*-norbornene acid.



Scheme 3.1 Synthesis of monomer **1**.

The ether functionalized Pd-pincer compound **8** was synthesized as outlined in Scheme 3.2. The starting compound, 5-octyloxy-isophthalic acid dimethyl ester, was

synthesized according to literature procedures[50] and was reduced with lithium aluminum hydride to yield the corresponding diol. The diol was then converted into the dichloride using methanesulfonyl chloride and the dichloride was coupled with an excess of sodium thiophenolate resulting in the formation of **14**, which on cyclopalladation with $Pd[PhCN]_2Cl_2$ and further workup, yielded the ether functionalized palladated pincer recognition unit, **8**.



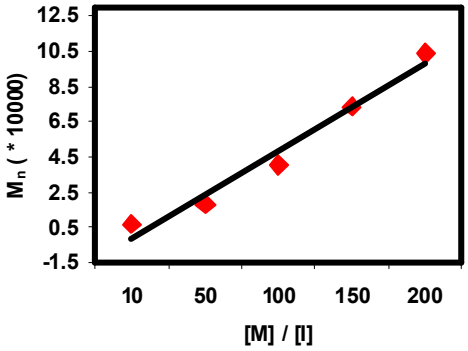
Scheme 3.2 Synthesis of the ether functionalized Pd pincer recognition unit **8**.

3.5 Homopolymerization studies

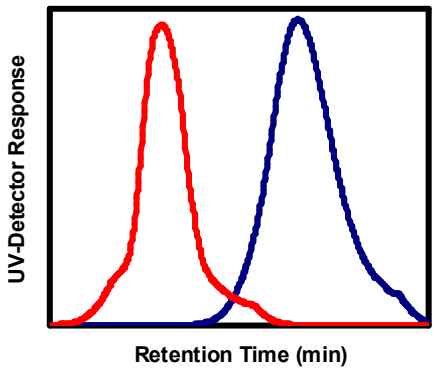
All polymerizations were carried out using Grubbs' first generation initiator in chloroform at room temperature.[43,40,51] The polymerizations were monitored by ^{1}H NMR analysis, and upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization. While the living polymerization of monomers **2**-**5** has been proven before,[43] **1** is a new monomer and its living character, a prerequisite for the formation of block copolymers had to be established.

Complete monomer conversion of **1** occurred in less than three hours depending upon the monomer-to-initiator ratios. This clearly indicates that Grubbs' first generation initiator is compatible with the terminal nitrile groups. This result was surprising since

nitriles have been known to act as ligands for the ruthenium metal center of the initiator, thereby preventing polymerization of such nitrile containing monomers.[52-55] However, monomers containing nitrile groups have been polymerized by ROMP before using tungsten initiator giving some precedent to our observation.[55] The favorable polymerization behavior of **1** using Grubbs first generation initiator might be related to the fact that 100% isomerically pure *exo*-monomer was used since it has been shown that *exo*-norbornene monomers have faster polymerization kinetics than their *endo* isomers.[43] To investigate the living nature of the polymerization, a series of polymerizations with variable monomer to initiator (M/I) ratios were carried out, and the resulting molecular weights were plotted against the M/I ratios. Figure 3.4 A shows a linear relationship between the M/I ratio and the molecular weights, indicating a controlled polymerization. Furthermore, the polydispersity index (PDI) depended upon the molecular weight of the polymers: at lower molecular weights the PDIs were higher with values being around 1.7, whereas the PDI decreased from 1.7 to 1.5 for the high molecular weight polymers suggesting a slower rate of initiation in comparison to the rate of propagation. Nevertheless, full initiation was observed within 120 seconds indicated by a complete shift of the carbene signal of the initiator in the ^{1}H NMR from 19.1 ppm before addition of the monomer to 18.0 ppm after complete initiation. No signal corresponding to the un-initiated initiator was observed.



A



B

Figure 3.4 Controlled polymerization of **1**. A) Plot of M_n versus the monomer-to-initiator ([M]:[I]) ratios. R^2 = 0.9698 B) GPC chromatographs of the block copolymer test of **1**: (blue curve) homopolymer after complete conversion ([M]:[I] = 20:1, M_w = 20,800, M_n = 11,700, PDI= 1.7), (red curve) the same polymer after the addition of 350 equivalents of monomer **5** ($[M_2]$:$[M_1]$ = 350:1, [M];[I] = 20, M_w = 346,000, M_n = 254,100, PDI= 1.3).

The living nature of the polymerization was unequivocally confirmed by a block copolymerization test. First, twenty equivalents of monomer **1** were polymerized. Upon complete conversion as monitored by ^{1}H NMR spectroscopy, 350 equivalents of monomer **5** were added. Complete conversion occurred within three hours. The homopolymer and the copolymer were characterized by gel-permeation chromatography (GPC) and the results are shown in Figure 3.4 B. The GPC trace of the block copolymer

is unimodal and shows a complete and dramatic shift to high molecular weight without traces of terminated low molecular weight polymer. This result in combination with the linear relationship between the M/I ratios and the molecular weight clearly proves the living nature of **1**.

3.6 Thymine monomer studies

Monomer **4** could be polymerized homogenously in chloroform only at low concentrations and low degrees of polymerization. At concentrations above 100 mg/mL and at degrees of polymerization above 25, phase separation occurred. Phase separation was also observed in dichloromethane and at elevated temperatures. These results clearly indicate that high molecular weight thymine homopolymers are not completely soluble in these solvents. However these polymers are soluble in polar solvents like THF. We rationalize that this phenomenon might be due to self-association of the functionalized thymines which can dimerize.[30] Hence, we carried out dimerization experiments and established the self-association constant of **4** in chloroform using ^{1}H NMR dilution experiments (Figure 3.5). The self-association constant of **4** was found to be 21 M^{-1}, which is close to the published literature value.[25]

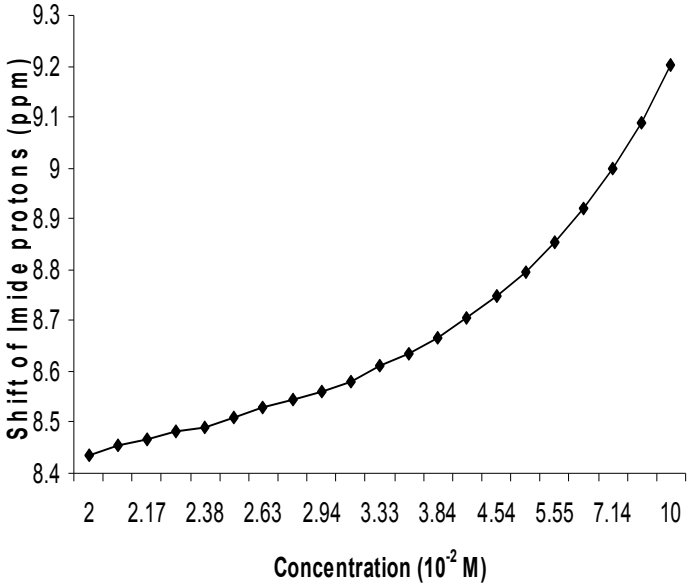


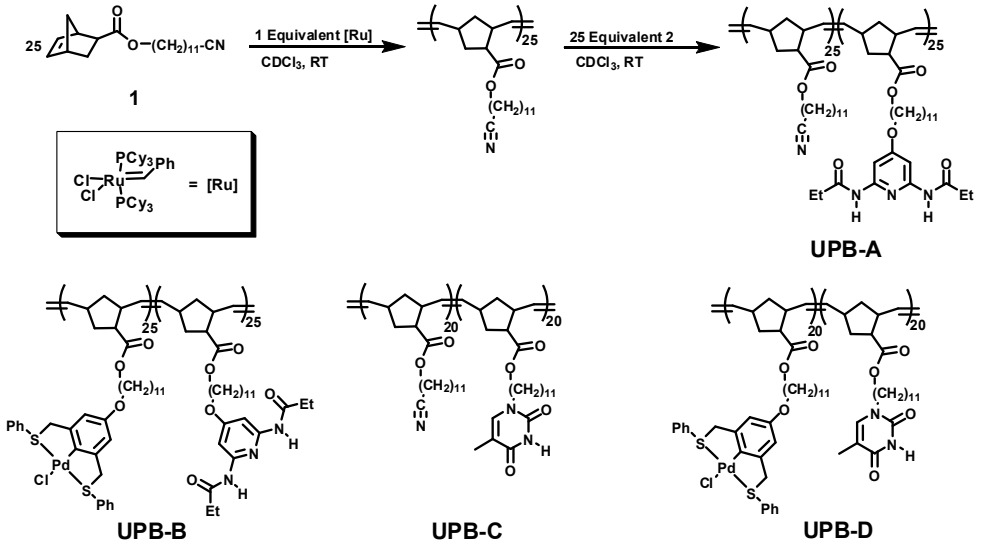
Figure 3.5 Chemical shift in ppm of the imide proton (N-H) of the thymine monomer (**4**) as a function of concentration in chloroform at room temperature.

Based on these results, the M/I ratios was limited to 20 for all copolymers containing **4** to ensure homogenous reaction conditions. Complete conversion of the ROMP of **4** occurred in about 30 minutes as monitored by ^{1}H NMR analysis and the GPC trace of the resulting homopolymer showed a unimodal signal with a narrow PDI of 1.12. We have previously reported that the ROMP of monomers **2** and **3** are living yielding polymers of narrow PDIs.[43]

3.7 Copolymerization studies

As monomer **1** could be polymerized in a living fashion, it was possible to synthesize block copolymers starting with any monomer. Four classes of di-block copolymers were synthesized containing one hydrogen bonding block and one metal coordination block (**UPB-A-D**). All block copolymerization were carried out by the sequential monomer addition after the first monomer was completely polymerized, as

determined by ^{1}H NMR spectroscopy analysis. The resulting block copolymers were characterized by GPC analysis, which showed unimodal distributions for all copolymers. In general, block copolymers containing **1** displayed higher PDIs around 1.7 while all other block copolymers (**UPB-B**, **UPB-D**) showed lower PDIs around 1.3 (Table 3.1). Scheme 3.3 outlines all block copolymers that have been synthesized for this study.



Scheme 3.3 Block copolymer formation using the synthesis of **UPB-A** as an example and the depiction of all synthesized di block copolymers. Polymer endgroups have been omitted for sake of clarity.

The GPC analyses of all homo and copolymers using THF as eluant are summarized in Table 3.1.

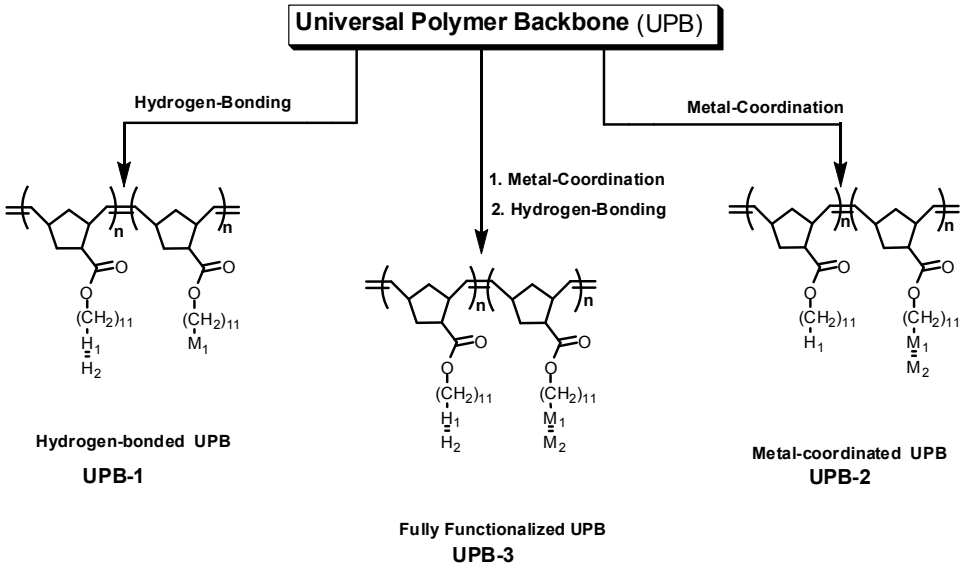
Table 3.1 Characterization of unfunctionalized homo and block copolymers. (a) Eluant: dichloromethane, (b) M/I ratios for each block. Polymer abbreviations are based on Scheme 3.3.

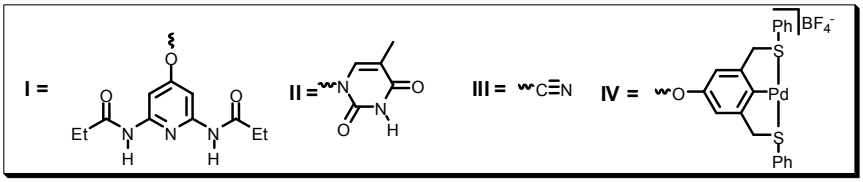
	[M]/[I]	M_n **(10^3)**	M_w **(10^3)**	**PDI**	T_g **(°C)**	T_{deg} **(°C)**

Poly-1	50	17.9	34.0	1.89	91	400
Poly-2	50	8.4	6.8	1.23	54	383
Poly-3[a]	50	30.6	36.1	1.17	79	299
Poly-4	20	3.9	4.4	1.12	69	387
UPB-A[b]	25	30.0	49.0	1.63	21	370
UPB-B[a,b]	25	11.4	15.8	1.30	48	255
UPB-C[b]	20	7.0	12.5	1.77	24	380
UPB-D[b]	20	21.6	29.4	1.36	44	376

3.8 Noncovalent functionalizations

Functionalization of the resulting block copolymers using noncovalent interactions as well as the investigation into the orthogonal character of all functionalization steps is key to our study. Therefore, after establishing the living nature of the polymerization of all monomers, the homopolymerization characteristics, and the synthesis of all block copolymers, the noncovalent functionalizations of all homo and block copolymers via hydrogen bonding and/or metal coordination were investigated. The self-assembly of a single block by using either hydrogen bonding or metal coordination was carried out as well as the stepwise multi-functionalization beginning with the metal coordination followed by hydrogen bonding was carried out as depicted in Scheme 3.4.





UPA	H_1	H_2	M_1	M_2
UPB-A-1	I	7	III	-
UPB-A-2	I	-	III	8
UPB-A-3	I	7	III	8
UPB-B-1	I	7	IV	-
UPB-B-2	I	-	IV	9
UPB-B-3	I	7	IV	9
UPB-C-1	II	6	III	-
UPB-C-2	II	-	III	8
UPB-C-3	II	6	III	8
UPB-D-1	II	6	IV	-
UPB-D-2	II	-	IV	9
UPB-D-3	II	6	IV	9

Scheme 3.4 Functionalization strategies of all block copolymers, "Universal Polymer Backbones". Polymer endgroups have been omitted for sake of clarity.

3.8.1 *Hydrogen bonding functionalization*

All homopolymers and copolymers were easily self-assembled via hydrogen bonding by simply stirring the polymer solution in dichloromethane with the appropriate complimentary recognition unit, followed by removal of the solvent under reduced pressure. Association constants (K_a values) of the monomers, homopolymers, and block copolymers were determined by ^{1}H NMR titration experiments in chloroform at room temperature (Table 3.2). We first investigated the K_a values of monomers **2** and **3**. The K_a value of the hydrogen-bonded complex between **2** and **7** was found to be 1080 M^{-1} whereas the K_a value between **4** and **6** was determined to be 920 M^{-1}. Both of these values are comparable to published literature values.[44,56] Upon polymerization, the K_a values of the homopolymers of both monomers (**Poly-2** and **Poly-4**) showed a significant decrease from 1080 M^{-1} to around 540 M^{-1} and from 920 M^{-1} to 460 M^{-1} for **Poly-2** and **Poly-4**, respectively. Similar decreases in the K_a values of hydrogen bonding monomers based on 2,6-diaminopyridines upon polymerization have been previously reported.[57]

Table 3.2 Association constants (K_a values in M^{-1}) for the self-assembly via hydrogen bonding of monomers **2** and **4**, all homopolymers and all block copolymers before and after metal coordination. 1: Errors for all K_a measurements ranged between 10 to 15%. Polymer abbreviations are based on Schemes 3.3 and 3.4.

Entry	K_a value[(1)]	Entry	K_a value[(1)]
2	1080	**UPB-A**	410
3	920	**UPB-A-2**	460
Poly-2 (50mer)	540	**UPB-B**	510
Poly-2 (100 mer)	540	**UPB-C**	370
Poly-4 (20 mer)	460	**UPB-C-2**	310
		UPB-D	340

Next the effect of molecular weight on the K_a by measuring the K_a values of a 100mer and a 50mer of **2** (Figure 3.6), was studied. For both polymers, the K_a values were found to be similar (540 M^{-1}) (Table 3.2) indicating the independence of the K_a from the polymer molecular weight. Similar results were obtained for monomer **4**.

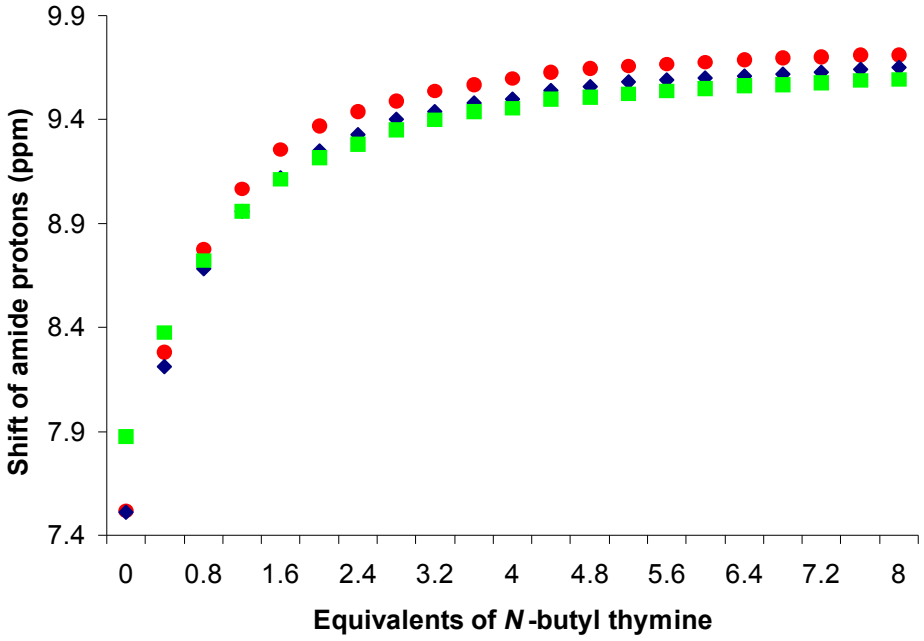


Figure 3.6 ^{1}H NMR spectroscopy titration curves for monomer **2** (red circles), a 50 mer of **2** (blue diamonds) and a 100 mer (green squares) of **2** with *N*-butyl thymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butyl thymine (0.01 M) in chloroform at room temperature.

After establishing the K_a values of the homopolymers, the K_a values of all block copolymers were determined and were compared to the corresponding monomers and homopolymers, in order to study the effect of block copolymerization on the hydrogen bonding interaction (Figures 3.7-3.9). In general, it was found that the K_a values of all block copolymers were comparable to their homopolymer analogs. Block copolymers

containing **2** had K_a values of 500 ± 50 M^{-1} while block copolymers based on **4** showed K_a values of 360 ± 50 M^{-1} (Figure 3.7). These results clearly prove that the block copolymerization had no significant effect on the stability of the hydrogen bonding complex. Furthermore, the K_a values are also independent of the comonomer used (either **1** or **3**) proving that the comonomer does not interfere with the hydrogen bonding, i.e. the hydrogen bonding step is orthogonal to the metal coordination sites in block copolymers.

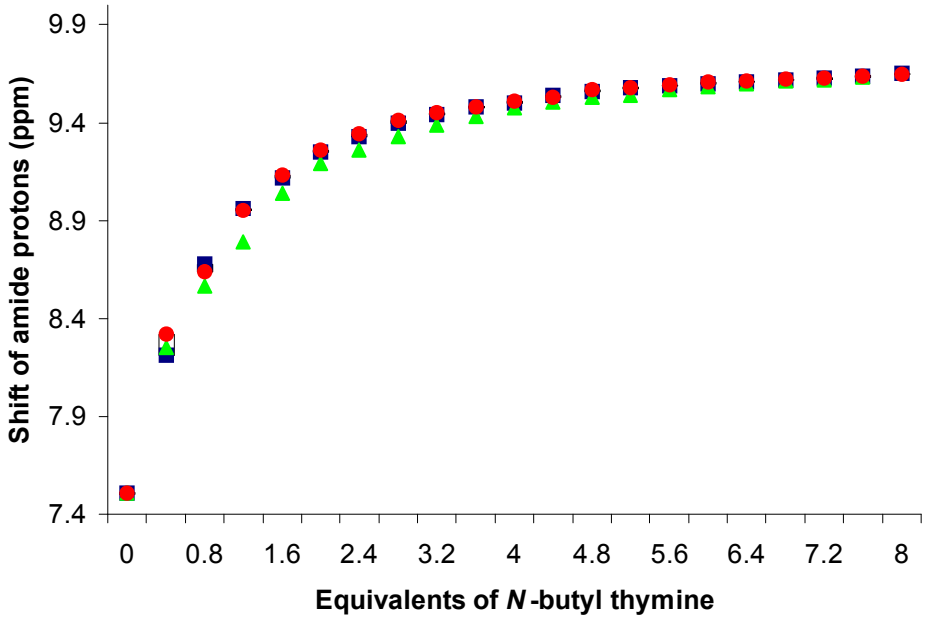


Figure 3.7 ^{1}H NMR spectroscopy titration curves for Poly-**2** (blue diamonds), **UPB-A** (green triangles) and **UPB-B** (red circles) with *N*-butyl thymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butyl thymine (0.01 M) in chloroform at room temperature.

To further study the effect of block copolymer composition on the K_a values, **UPB-A** was synthesized with three different ratios of block A to block B (ratios of 25:75, 50:50 and 75:25 of **1**:**2**) and the K_a values of each block copolymer were determined (Table 3.2 and Figure 3.8). The K_a values of these different block copolymer

compositions were found to be identical within the experimental error indicating that the block copolymer composition had little effect on the K_a values.

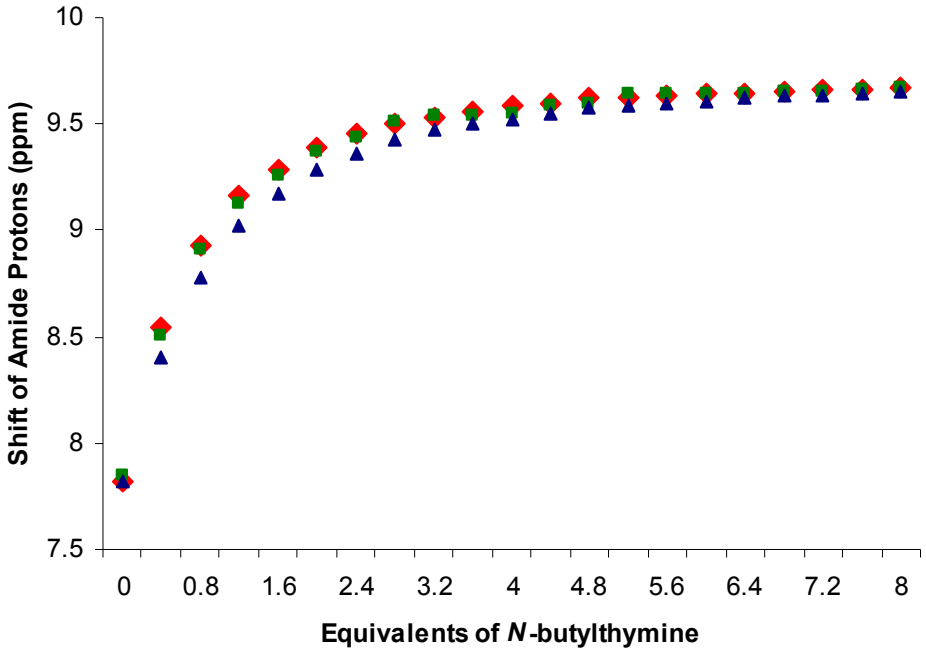


Figure 3.8 ^{1}H NMR spectroscopy titration curves for **UPB-A** (25/75) (red diamonds), **UPB-A** (50/50) (green squares) and **UPB-A** (75/25) (blue triangles) with *N*-butyl thymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butyl thymine (0.01 M) in chloroform at room temperature.

3.8.2 *Effect of the dimerization of the thymine functional groups*

The block copolymers **UPB-A** and **UPB-B** are identical to **UPB-C** and **UPB-D** but for the terminal hydrogen bonding units (**UPBs A** and **B** are based on 2,6-diaminopyridine while **UPBs C** and **D** on thymine). Nevertheless, both terminal hydrogen bonding units are complementary to each other consisting of identical ADA-DAD units, hence it is expected that the K_a values for all polymers be similar. However, the K_a values of all block copolymers containing **4** are significantly lower (about 10-30%) than those containing **2**. These lower association constants can be attributed to the dimerization of the thymine groups attached to the polymer backbone thereby lowering

the association constant. In contrast, block copolymers based on **2** have low propensity to dimerize resulting in higher association constants.[57]

3.8.3 *Metal coordination*

The terminal nitrile functionalized monomers and polymers as well as the palladated pincer complex functionalized monomers and polymers represented a complimentary set of a metal coordination system. Functionalization of the pincer moieties in both cases began with the abstraction of the chlorine atom from the palladated center using $AgBF_4$ followed by coordination of the appropriate ligand to the palladium atom.[18] The nitrile functionalized polymers in essence act as a "polymeric ligand" that can coordinate with the Pd pincer center **8** whereas the covalent functionalization of the pincer complex onto the polymer can be seen as a "polymeric metal center" which needs to be activated prior to functionalization. The functionalization of the nitrile-based polymers was significantly easier and could be carried out in analogy to literature procedures in a variety of solvents including chloroform and dichloromethane.[58] However every attempt to coordinate the pincer block copolymers in chloroform resulted in immediate precipitation. Furthermore, polar solvents such as DMF and DMSO could not be employed because of the severe disruption of the hydrogen bonding complex formation of the block containing the hydrogen bonding recognition units. Therefore, the metal coordination of the pincer based block copolymers (**UPBs B** and **D**) was successful only in anhydrous dichloromethane using a saturated solution of $AgBF_4$ in an equivolume mixture of nitromethane and acetonitrile. This important difference can be ascribed to the fact that during the metal coordination step, the pincer functionalized block copolymer gets converted into a "polyelectrolyte species" thus decreasing the solubility

of the system in a non-polar environment, whereas in the case of the nitrile functionalized block copolymers, the Pd pincer center **8** get positively charged on activation thereby circumventing the formation of a "polyelectrolyte species". Nevertheless, when using an appropriate solvent, quantitative metal coordination took place and no interferences of the hydrogen bonding moieties during the metal coordination steps were observed using ^{1}H NMR spectroscopy.[59]

3.8.4 *Multi-functionalizations*

After establishing that a) the metal coordination steps on all homo and block copolymers can be carried out quantitatively within seconds without interference of the hydrogen bonding recognition motifs and b) the strength of the hydrogen bonding interaction is independent of the copolymers used, multi-functionalization experiments were carried out. In particular, the K_a value was determined via ^{1}H NMR titration experiments of block copolymers that were first functionalized via metal coordination. As can be seen in Figure 3.9 and Table 3.2, similar K_a values for the hydrogen bonding titration experiments for all metal-coordinated block copolymers were observed as described above for all single hydrogen bonding functionalization studies on homopolymers and block copolymers (the K_a values range from 460 M^{-1} for block copolymers containing **2** to 360 M^{-1} for block copolymers containing **4**). These results clearly demonstrate that metal coordination does not interfere with the hydrogen bonding functionalization, i.e. both recognition motifs are orthogonal to each other in all block copolymers. However, due to poor solubility, it was possible to measure the K_a values for **UPB-B-2** and **UPB-D-2**.

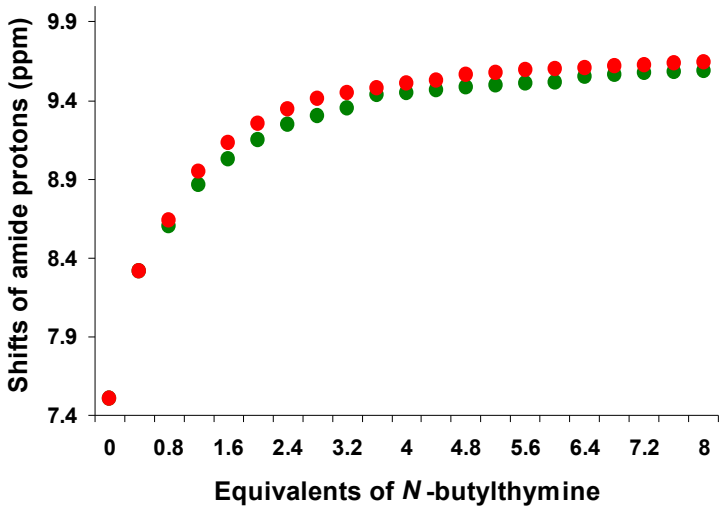


Figure 3.9 ^{1}H NMR spectroscopy titration curves for **UPB-A** (red circles), **UPB-A-2** (green circles) with *N*-butyl thymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butyl thymine (0.01 M) in chloroform at room temperature.

3.9 Thermal characterization

To study the effect of the noncovalent functionalization on the thermal properties of all polymers, the glass-transition temperatures (T_g) and onset temperatures of degradation (T_{deg}) of all homo and block copolymers were measured. The results are tabulated in Table 3.3. **Poly-1** displayed the highest T_g as well as T_{deg} values, which can be explained by the strong inter- as well as intra- molecular dipole-dipole interactions between the nitrile groups, as reported for other nitrile-based polymers such as poly(acrylonitrile).[60] **Poly-1** upon metal coordination with **8** gave the self-assembled **Poly-1(SA)** which exhibited a large decrease in the T_g due to the disruption of these intermolecular interactions. **Poly-1(SA)** also showed a large decrease in the thermal stability, which can be explained by the introduction of metallic species into the system. Similarly, **Poly-3**, a metallated polymer, showed the lowest thermal stability as compared

to the other non-metal containing polymers, this can be explained by the fact that metal residues catalyze the thermal degradation of polymers.[61,62] **Poly-3** upon functionalization by either pyridine or functionalized nitriles gave self-assembled **Poly-3(SA)** which did not exhibit significant changes in the T_g. However, upon metal coordination with **9**, **Poly-3(SA)** showed a large decrease in the thermal stability. **Poly-4**, which is able to undergo a high degree of intermolecular interactions via hydrogen-bonding, exhibited a large decrease in the T_g values after functionalization with **6** to give self-assembled **Poly-4(SA),** however the thermal stability was not affected. **Poly-2** on self-assembly with **7** gave the self-assembled **Poly-2(SA)** showed a large decrease in both, the T_g and T_{deg}.

Table 3.3 Thermal characterization data of all self-assembled homo and block copolymers. Polymer abbreviations are based on Schemes 3.3 and 3.4.

Polymer	T_g (°C)	T_{deg} (°C)	Polymer	T_g (°C)	T_{deg} (°C)
Poly-1(SA)	72	185	**UPB-B-2**	31	190
Poly-2(SA)	10	278	**UPB-B-3**	33	222
Poly-3(SA)	64	194	**UPB-C-1**	13	320
Poly-4(SA)	36	383	**UPB-C-2**	5	284
UPB-A-1	6	265	**UPB-C-3**	2	284
UPB-A-2	6	240	**UPB-D-1**	29	312
UPB-A-3	10	232	**UPB-D-2**	42	205
UPB-B-1	32	227	**UPB-D-3**	30	230

All block copolymers displayed lower glass-transition temperatures than their homopolymer counterparts although their T_{deg} were similar. To understand the individual

effects of hydrogen bonding and metal coordination interactions on the thermal properties of the copolymers, the glass-transition temperature and onset of thermal degradation after each functionalization step was measured. Both functionalizations, hydrogen bonding and metal coordination, decreased the T_g of the copolymers, by similar extents, although the fully functionalized copolymers had lower T_g due to the combined effects of both functionalizations. The decrease in the T_g values upon functionalization can be explained by the plasticization of the polymers. Similarly, the polymers, upon metal coordination, had lower onsets of degradation temperatures. It can be seen in every case that the thermal stability decreases to a higher extent upon metal coordination as compared to their corresponding hydrogen bonded counterparts.

3.10 Summary and conclusions

In this chapter, di-block copolymers possessing both hydrogen bonding and metal coordination recognition units have been synthesized using ROMP. The hydrogen bonding recognition system consisted of substituted thymines and 2,6-diaminopyridines whereas the metal coordination system consisted of palladated SCS pincer complexes and functionalized nitriles and pyridine. The effect of degree of polymerization, block copolymer composition and most importantly metal coordination on the noncovalent functionalization via hydrogen bonding was studied in detail. It was found that none of these variables had any substantial impact on the stability of the hydrogen-bonded complexes. These results suggest that the investigated noncovalent interactions are orthogonal in block copolymers, a prerequisite to employ this strategy in material science. Finally the effects of these noncovalent functionalizations on the thermal properties of the polymers were studied. It was found that both functionalization by

hydrogen bonding and metal coordination decrease the glass-transition temperatures of all polymers due to disruption of the intermolecular forces and similarly the functionalized polymers had lower thermal stability than their corresponding unfunctionalized counterparts.

In summary, it has been demonstrated that combining a highly functional group tolerant polymerization route with noncovalent functionalization techniques, allows for the facile syntheses of highly functionalized materials having a high degree of control over their molecular structure. Using noncovalent interactions such as hydrogen bonding and metal coordination one can synthesize from a single polymer backbone ("Universal Polymer Backbone") a large variety of functionally varied polymers, which widely differ in their physical and chemical properties, simply by altering the functionalization strategy.

3.11 Experimental section

General

All reagents were purchased either from Acros Organics, Aldrich or Strem Chemicals and used without further purification unless otherwise noted. Dimethylformamide (DMF) 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. N-(6-Propionylamino-pyridin-2-yl)-propionamide,[44] *N*-butyl thymine,[57] isomerically pure *exo*-norbornene acid,[45,54] 12-bromododecanitrile,[47] 5-Octyloxy-isophthalic acid dimethyl ester [48] and monomers **2**,[43] **3**,[43] **4**,[63] and **5**[17] were synthesized according to published procedures.

Characterization procedure

^{1}H NMR and ^{13}C NMR spectra were taken using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Abbreviations used include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), and unresolved multiplet (m). Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility on a VG-70se spectrometer using electron impact ionization (EI). Self-CI denotes self-chemical ionization. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Gel-permeation chromatography (GPC) analyses were carried out using a Shimadzu pump, a Shimadzu UV detector with tetrahydrofuran (THF) or dichloromethane 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. The glass-transition temperature of the polymers (T_g) was measured by differential-scanning calorimetry (DSC). The DSC analyses were performed under an atmosphere of nitrogen using a Mettler Toledo DSC 822e, which was calibrated using Indium standards. The temperature program provided two heating and cooling cycles between -100 and 100˚C at 10˚C /min, with the sample size ranging from 5 to 9 mg. The onset of thermal degradation for the polymers (T_{deg}) was measured by thermal gravimetric analysis (TGA). The TGA analyses were performed under an atmosphere of nitrogen using a Shimadzu TGA-50 and all samples were heated from 25 to 450˚C at a rate of 10˚C /min.

***exo*-Bicyclo [2.2.1] hept-5-ene-2-carboxylic acid 11-cyano-undecyl ester (1)**

Exo-bicyclo [2.2.1] hept-5-ene-2-carboxylic acid (4.4 g, 0.021 mol) and compound **10**[49] (4.16 g, 0.021 mol) were dissolved and stirred in anhydrous dichloromethane (100 mL). Dicyclohexyl dicarbondiimide (DCC) (4.4 g, 0.021 mol) in dichloromethane and a catalytic amount (20 mg) of 4-dimethylaminopyridine (DMAP) were added at room temperature. Immediately a white precipitate was formed. The mixture was refluxed for twelve hours after which it was cooled and filtered. The solution was then concentrated and purified by column chromatography (SiO_2, eluant: dichloromethane), and dried on high vacuum to yield **1** as a colorless liquid (5 g, 75%). ^{1}H NMR ($CDCl_3$): δ = 6.09 (m, 2H, CH=CH), 4.06 (t, 2H, *J* = 6.67 Hz, -$COOCH_2$-), 3.00 (s, 1H), 2.88 (s, 1H), 2.31 (2H, t, *J* = 7.08 Hz, -CH_2-CN), 2.17 (m, 1H), 1.899 (m, 1H), 1.67-1.55 (m, 4H), 1.51-1.25 (m, 20H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 138.0, 135.8, 119.2, 64.6, 46.8, 46.5, 43.4, 41.8, 30.55, 29.6, 29.6, 29.5, 29.4, 29.0, 28.9, 28.9, 26.2, 25.6, 17.3. HRMS (Self-CI) *m/z* (100%) = 318.2393 (M^+, calcd 318.2348). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84; Found: C, 75.49; H, 9.93.

(3-Hydroxymethyl-5-octyloxy-phenyl)-methanol (12)

5-Octyloxy-isophthalic acid dimethyl ester [48] (**11**) (7.1 g, 0.022 mol) was dissolved in anhydrous THF and added to a suspension of $LiAlH_4$ (1.66 g, 0.044 mol) in THF at 0˚C. The reaction was stirred at room temperature for twelve hours after which the THF was removed under reduced pressure. The residue was carefully acidified by adding 1N HCl dropwise at 0˚C to dissolve the $LiAlH_4$. The solution was then extracted with dichloromethane (3 x 200 mL), the organic extracts were dried with $MgSO_4$ and the solvent removed under reduced pressure to yield a white solid (6.00 g, 86%). ^{1}H NMR ($CDCl_3$): δ = 6.91 (s, 1H, ArH), 6.83 (s, 2H, ArH), 4.64 (s, 4H, -CH_2OH), 3.94 (t, 2H, *J* =

6.38 Hz, -OCH_2-), 1.93 (broad, 2H, -OH), 1.75 (m, 1H,), 1.44 (m, 2H), 1.29 (m, 8H), 0.87 (distorted t, 3H, *J* = 6.8 Hz, -CH_3). ^{13}C NMR ($CDCl_3$): δ = 159.3, 142.8, 117.6, 112.1, 68.3, 64.9, 64.8, 32.0, 29.7, 29.6, 26.4, 23.0, 14.5. MS (EI) *m/z* (100%) = 266.18 (M^+, calcd. 266.19). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84; Found: C, 72.17; H, 9.86.

1, 3-Bis-chloromethyl-5-octyloxy-benzene (13)

Compound **12** (4.99 g, 0.019 mol) and trimethyl amine (5.68 g, 0.056 mol) were dissolved in 100 mL of anhydrous dichloromethane and cooled to 0˚C. Methane sulfonyl chloride (6.43 g, 0.056 mol) was added dropwise over a period of one hour. After complete addition, the reaction mixture was gradually heated to 38˚C for twelve hours. The reaction mixture was then washed with 1N NaOH (50 mL), 1N HCl (50 mL) and water (100 mL), and finally dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, eluant: hexanes-dichloromethane 3/2, v/v) to yield a colorless liquid (3.94 g, 70%). ^{1}H NMR ($CDCl_3$): δ = 6.98 (s, 1H, ArH), 6.89 (s, 1H, ArH), 4.54 (s, 4H, -CH_2Cl), 3.94 (t, 2H, *J* = 6.50 Hz, -OCH_2-), 1.80 (p, 2H, *J* = 6.64 Hz, -OCH_2CH_2-), 1.48 (m, 2H), 1.34 (m, 8H), 0.92 (distorted t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ = 159.7, 139.4, 120.8, 114.8, 68.4, 46.2, 32.2, 29.7, 29.6, 29.5, 26.4, 23.0, 14.5. MS (EI) *m/z* (100%) = 302.12 (M^+, calcd. 302.12). Anal. Calcd for $C_{16}H_{24}Cl_2O$: C, 63.37; H, 7.98; Found: C, 63.72;H, 8.00.

1, 3-Bis [(phenylsulfanyl) methyl]-5-octyloxy-benzene (14)

Sodium thiophenolate (7.10 g, 0.051 mol) was dissolved in anhydrous THF (100 mL) and dichloride **13** (3.94 g, 0.012 mol) was added drop wise to the reaction mixture at room temperature. The mixture was then heated at 50˚C for twelve hours, after which the

solvent was removed under reduced pressure and the crude mixture was redissolved in dichloromethane (200 mL). The solution was then washed with brine (100 mL), 2 N NaOH (100 mL), water (100 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, eluant: hexanes-dichloromethane 7/3, v/v) to yield the product as a colorless liquid (3.94 g, 70%). ^{1}H NMR ($CDCl_3$): δ = 7.30-7.15 (m, 10H, -SC_6H_5), 6.85 (s, 1H, ArH), 6.70 (s, 2H, ArH), 4.03 (s, 4H, -SCH_2-), 3.84 (t, 2H, *J* = 6.57 Hz, -OCH_2-), 1.72 (m, 2H, -OCH_2CH_2-), 1.43-1.29 (m, 10H, -$(CH_2)_5$-), 0.89 (distorted t, 3H, *J* = 7.10 Hz, -CH_3). ^{13}C NMR ($CDCl_3$): δ = 159.8, 139.4, 137.2, 129.4, 127.7, 127.4, 120.8, 114.9, 68.5, 46.2, 32.2, 29.8, 29.7, 29.6, 26.4, 23.1, 14.6. MS (EI) *m/z* (100%) = 450.20 (M^+, calcd. 450.21). Anal. Calcd for $C_{28}H_{34}OS_2$: C, 74.62; H, 7.60; Found: C, 74.64; H, 7.69.

Pd-Cl 1, 3-Bis[(phenylsulfanyl)methyl]-5-octyloxy-benzene (8)

Compound **14** (400 mg, 0.89 mmol) was dissolved in a mixture of dichloromethane (5 mL) and acetonitrile (10 mL) and placed under an atmosphere of argon. $Pd[(C_6H_5CN)_2Cl_2]$ (340 mg, 0.89 mmol) was added to the stirred solution. The resulting orange solution was stirred for 30 min, after which $AgBF_4$ (425 mg, 2.19 mmol) was added in one portion. Immediately, the orange solution became pale yellow due to the formation of silver chloride and the solution was stirred for 30 min under argon. The reaction mixture was then diluted by dichloromethane (250 mL) and the solution was poured into a saturated aqueous solution of NaCl and stirred vigorously for eight hours. The organic layer was separated, dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification by column chromatography (SiO_2, eluant: dichloromethane-methanol 99/1, v/v) gave **8** as a yellow solid (400 mg, 77%). ^{1}H NMR

(CD_2Cl_2): δ = 7.80 (m, 4H, -SC_6H_5), 7.43 (m, 6H, -SC_6H_5), 6.61 (s, 2H, ArH), 4.59 (bs, 4H, -SCH_2-), 3.85 (m, 2H, -OCH_2-), 1.74 (m, 2H, -OCH_2CH_2-), 1.45-1.30 (m, 10H, -$(CH_2)_5$-), 0.88 (m, 3H, -CH_3). ^{13}C NMR ($CDCl_3$): δ = 220.2, 157.2, 150.3, 132.6, 131.6, 129.9, 129.8, 109.0, 68.3, 51.9, 32.0, 29.5, 29.4, 29.4, 26.2, 22.8, 14.3. HRMS (EI) *m/z* (97.12 %) = 590.06 (M^+, calcd 590.05). Anal. Calcd for $C_{28}H_{33}ClOPdS_2$: C, 57.96; H 6.32, Found: C, 56.68; H, 5.75.

Polymerizations

The monomers were dissolved in an appropriate volume of dry distilled deuterated chloroform. The calculated amount of a stock solution of Grubb's first generation initiator in chloroform was added in one portion. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy. Upon complete polymerization, a drop of ethyl vinyl ether was added to terminate the polymerization. In the case of copolymerizations, upon complete conversion of the first monomer, the second monomer was added in chloroform. Purification of all polymers was performed by precipitating the polymers from ice-cold methanol and repeated washings with ice-cold methanol and ice-cold hexanes, followed by prolonged drying at room temperature under high vacuum.

Poly-1 ^{1}H NMR ($CDCl_3$): δ = 5.34-5.18 (m, 2H, CH=CH), 4.01(t, 2H, *J* = 6.18 Hz, -$COOCH_2$-), 2.68 (br m, 2H), 2.48 (br m, 2H), 2.31 (t, 2H, *J* = 7.08 Hz, -CH_2-CN), 2.02-1.91 (br m, 2H), 1.60 (br m, 5H), 1.41 (br m, 2H), 1.25 (br s, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 134-131, 120, 64.67, 50-49, 47.8, 43.2, 42.1, 41.3, 37.2, 36.4, 29.5, 28.9, 29.1, 25.5.

Poly-4 ^{1}H NMR (THF-d4): δ = 9.26 (s, 1H, -NH-), 6.12 (s, 1H, thymine), 4.30-4.10 (br m, 2H, CH=CH), 2.91 (t, 2H *J* = 5.98 Hz, -$COOCH_2$-), 2.75 (m, 1H), 2.52 (t, 2H, *J* = 7.29 Hz, -CH_2-N), 1.9-1.58 (m, 1H), 1.6-1.42 (br m, 2H), 0.71-0.5 (m, 10H), 0.20 (br s, 12H, alkyl chains). ^{13}C NMR (THF-d4): δ = 178.6, 167.8, 154.8, 144.2, 138.8, 137.3, 136.4-135.1, 113.0, 111.9, 82.5, 81.7, 67.7, 53.5, 51.5, 45.9, 44.9, 43.8, 41.0, 33.3, 32.9, 31.4, 30.5, 29.8, 28.5.

UPB-A ^{1}H NMR ($CDCl_3$): δ = 8.19 (s, 2H, -NH-), 7.49 (s, 2H, Pyr_β), 5.32-5.17 (br m, 4H, CH=CH), 4.1 (br s, 4H, -$COOCH_2$-), 3.99 (br m, 2H, -OCH_2-), 2.64 (br m, 8H), 2.47 (br m, 4H, -$COOCH_2CH_3$), 2.34 (t, 2H, *J* = 7.1 Hz, -CH_2-CN), 2.16 (s, 6H), 2.01-1.9 (br m, 8H), 1.67-1.57 (br m, 20 H), 1.24-1.1 (br m, 92H, alkyl chains). ^{13}C NMR ($CDCl_3$): δ = 176.3, 172.9, 150.4, 133.9, 131.5, 120.1, 96.2, 69.7, 68.6, 64.7, 50.4, 49.7, 47.8, 42.1, 41.2, 37.1, 36.4, 35.0, 32.0, 30.8, 29.7, 29.5, 29.0, 28.8, 26.0, 25.5, 17.3, 9.5.

UPB-B ^{1}H NMR (CD_2Cl_2): δ = 8.10(s, 2H, -NH-), 7.80 (br m, 4H, -SC_6H_5), 7.49 (br s, 2H,Pyr_β), 7.33 (br m, 8H, -SC_6H_5), 6.54 (s, 2H, ArH), 5.32-5.16 (br m, 4H, CH=CH), 4.50 (br s, 4H, -SCH_2-), 4.00 (br m, 6H, -$COOCH_2$-), 3.82 (t, 4H, *J* = 6.22 Hz, -OCH_2-), 2.63 (br m, 4H, bridging proton), 2.44 (br m, 4H, bridging proton), 2.36 (br m, 4H, -$COOCH_2CH_3$), 2.16 (br s, 2H), 2.02-1.91 (br m, 4H), 1.69 (br m, 4H), 1.56 (br m, 4H), 1.24-1.16 (br m, 46H, alkyl chains). ^{13}C NMR ($CDCl_3$): δ = 176.5, 172.9, 169.2, 157.2, 151.6, 150.8, 150.3, 132.6, 131.5, 129.9, 109.0, 96.2, 69.7, 68.6, 64.7, 54.0, 51.0, 32.0, 30.8, 29.7, 29.4, 28.9, 26.0.

UPB-C ^{1}H NMR (CD_2Cl_2): δ = 9.2(s, 1H, -NH-), 6.14 (s, 1H, thymine proton), 5.03 (br s, 1H, CH=CH), 4.33 (br m, 4H, -$COOCH_2$-), 4.12 (br m, 1H, -CH_2-N), 2.92 (br m, 6H), 1.63-1.46 (t, 14H), 1.27 (t, 2H, *J* = 7.00 Hz), 0.94 (br m, 2H), 0.84 (br m, 4H), 0.71 (br s,

4H), 0.64 (br s, 4H), 0.51 (br m, 16H), 0.23 (br m, 48H, alkyl chains). ^{13}C NMR ($CDCl_3$): δ = 178.4, 167.6, 154.7, 144.0, 139.4, 137.36, 136.5-135.2, 131.9, 122.9, 112.9, 67.7, 53.2, 51.2, 48.6, 46.0, 45.4, 44.9, 40.0, 33.4, 32.8, 30.3, 29.8, 29.3, 20.0.

UPB-D ^{1}H NMR (CD_2Cl_2): δ = 10.13 (s, 1H, -NH-), 7.83 (br m, 4H, $-SC_6H_5$), 7.39 (br m, 6H, $-SC_6H_5$), 7.04 (br m, 1H, ArH), 6.57 (br s, 1H, thymine proton), 5.37-5.2 (br m, 4H, CH=CH), 4.57 (br s, 4H, $-SCH_2-$), 4.01 (br m, 4H, $-COOCH_2-$), 3.85 (br m, 2H, $-OCH_2-$), 3.67 (t, 2H, J = 7.08 Hz, $-CH_2-N$), 2.67-2.48 (br m, 2H), 1.88 (br m, 4H), 1.63-1.57 (br m, 10H), 1.27 (br m, 32H, alkyl chains). ^{13}C NMR (CD_2Cl_2): δ = 177.7, 166.9, 159.1, 153.6, 152.2, 142.8, 134-131, 112.2, 110.9, 70.2, 66.4, 50.5, 44.2, 38.3, 31.7, 30.8, 28.5, 14.1.

Self-assembly experiments

Hydrogen Bonding:

The polymers (100 mg) were dissolved in dry dichloromethane (5 mL) until a homogenous solution was obtained. Then, the calculated amount of the hydrogen bonding recognition unit dissolved in dry dichloromethane (2-3 mL) was added in one portion and the solution was stirred for 30 min after which the solvent was removed under reduced pressure to yield the hydrogen bonded polymer.

Metal Coordination:

The polymers were dissolved in dry dichloromethane (5 mL) until a homogenous solution was obtained. Then the calculated amount of **8**-**9**, dissolved in dry dichloromethane (2-3 mL), was added. The reaction mixture was stirred and $AgBF_4$ (aq) was added, whereas for the pincer based polymers, an equivolume solution (0.02 mL) of nitromethane and acetonitrile was used to dissolve the $AgBF_4$. After one minute, the

solution turned green and AgCl precipitated. The solution was then allowed to stir for one hour. The reaction mixture was filtered through Celite and then the solvent was removed under reduced pressure, to yield the metal coordinated polymers as light green solids.

Titration experiments:

^{1}H NMR spectroscopy titration association constants were measured by ^{1}H NMR spectroscopy titration of a 0.005 M solution of the polymer (based on the hydrogen bonding moieties) in $CDCl_3$ with a 0.01M of the corresponding receptor moiety. The chemical shifts of the amide protons for the 2,6-diaminopyridines and the imide protons of the substituted thymines were monitored. The ^{1}H NMR spectroscopy data was evaluated by ChemEquili software to calculate the association constants.[64] The errors ranged from 10 to 15%.

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CHAPTER FOUR

Noncovalently Functionalized Poly(norbornene)s Possessing both Hydrogen Bonding and Coulombic Interactions

4.1 Abstract

Random copolymers containing both hydrogen bonding and charged ionic sites have been synthesized by the ROMP of norbornene monomers containing either an ionic quaternary ammonium group or a 2,6-diaminopyridine functionality. All copolymers were functionalized subsequently via self-assembly using hydrogen bonding and Coulombic interactions. The hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine were studied in the presence of the ionic quaternary ammonium group and it's subsequent self-assembly with three different charged anionic species was investigated to determine the influence of the Coulombic interactions on the strength of hydrogen bonding. Both qualitative analysis using IR and ^{1}H NMR spectroscopy techniques and quantitative analysis using ^{1}H NMR spectroscopy titrations were carried out. It was found that hydrogen bonding was independent of the nature and presence of the Coulombic interactions in chloroform as the solvent. These results prove that the studied hydrogen bonding interactions are orthogonal to the Coulombic interactions and that both interactions can be used independently of each other in the same system to noncovalently functionalize polymer backbones.

4.2 Introduction

In the previous chapters it has been explained that that side-chain polymer functionalization through noncovalent chemistry has been shown to have several distinct advantages over covalent functionalization strategies, such as fast and facile functionalization, reversibility, and self-reparability.[1-3] One example from the work of Ikkala *et al.*, demonstrates that by combining metal coordination and ionic interactions with polymer science, highly controlled and functionalized nanostructures can be synthesized in a straight forward fashion.[4] Coulombic interactions are among the most widely encountered noncovalent interactions rivaled only by hydrogen bonding and van der Vaals interactions in their frequency. One important strategy for noncovalent multi-functionalization[5,6] would be the controlled employment of ionic interactions along with other noncovalent interactions within the same polymeric system. Such a strategy would allow for the tailoring of materials properties by exploiting the differences in the nature of these reversible interactions as well as multi-functionalization.[7,8] However, a prerequisite for the use of multiple interactions in such a system is that all noncovalent interactions have to be orthogonal to each other, or at least the effects of one interaction in the presence of the other one must be clearly understood. Chapter three reported the detailed investigations into the orthogonality of hydrogen bonding and metal coordination[9,8] where it was proven that these two interactions can be used in an orthogonal fashion expanding the possibility to design polymers that can be utilized as precursors for a variety of materials applications through simple self-assembly based functionalization.[7,8] Although there have been some reports where Coulombic interactions have been used in the presence of hydrogen bonding in polymeric systems, a

study of the interdependence of these two interactions with a quantitative evaluation is lacking.[10,11] Furthermore, Rotello and coworkers have used hydrogen bonding and Coulombic self-assembly in micro-patterning surfaces, however the recognition units were present on separate polymer backbones.[12] This chapter demonstrates the efficiency of direct copolymerization via ROMP of functionalized monomers as a convenient route to multi-functionalized polymers having both hydrogen bonding and Coulombic self-assembly sites.

While ROMP of charged metal complexes such as ferrocene[13-17] and in ionic liquids as solvents[18] has been carried out, there are only few reports of polymerizing charged monomers.[19-21] The vast majority of reports utilize post polymerization modifications to yield polyelectrolytes.[22-26] However, such post polymerization modifications can involve side-reactions such as hydrolysis, chain-degradation, or cross-linking thereby leading to ill-defined structures.[27] By directly copolymerizing a charged monomer, post-polymerization steps can be avoided, giving a straightforward and robust method to make functional materials such as ionomers and polyelectrolytes. This chapter, reports the first synthesis of a highly functionalized polymer by copolymerizing a charged norbornene monomer with a norbornene monomer containing a terminal hydrogen bonding motif using ROMP followed by a detailed investigation into the noncovalent multi-functionalization of the resulting copolymers as shown schematically in Figure 4.1.

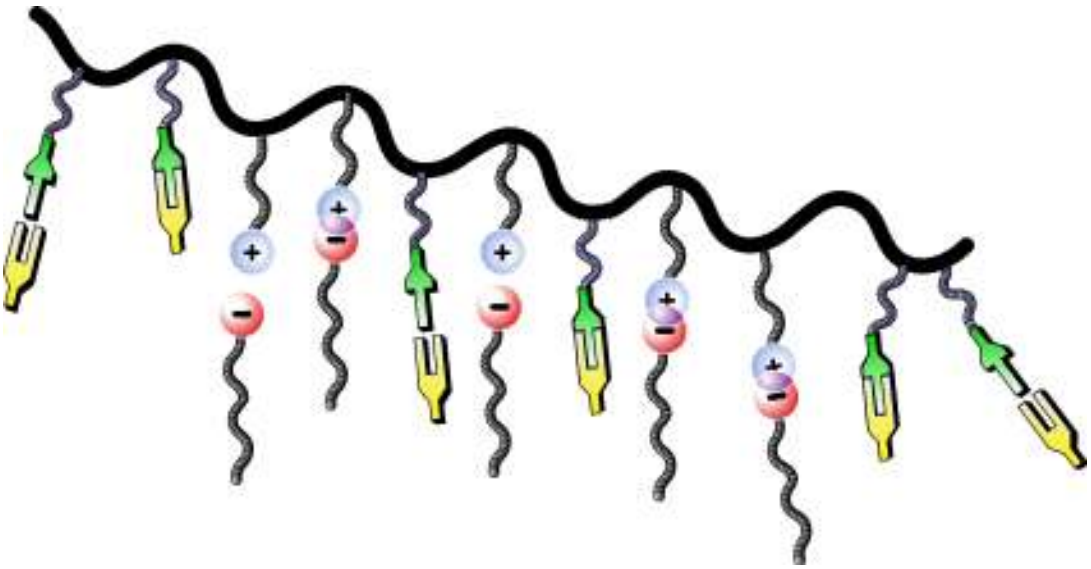


Figure 4.1 A cartoon depiction of a random copolymer noncovalently multi-functionalized by complementary sets of recognition units based on hydrogen bonding and Coulombic self-assembly.

4.3 Research design

The research design consists of multi-functional random copolymers having both hydrogen bonding and Coulombic recognition sites. These multi-functionalized copolymers can be viewed as "Universal Polymer Backbones"[7,8] since a family of different functionalized polymeric materials can be obtained from a single polymer backbone by varying the complementary recognition units, i.e. the functionalization. These polymer backbones are based on monomers that are comprised of a norbornene moiety that can be polymerized using ROMP and a long alkyl spacer composed of either a C-10 or C-11 chain to improve solubility and to decouple the recognition units from the polymer backbone. In particular, functionalized 2,6-diaminopyridines (DAD) and *N*-butylthymine (ADA) (Figure 4.2) have been employed. The 2,6-diaminopyridine recognition units are anchored onto the polymer backbone with *N*-butylthymine being the complementary recognition unit. In Chapter three, it was shown that higher K_a are

achieved with the 2,6-diaminopyridines being attached to the polymer backbone as they have a lesser tendency to undergo self-association as compared to their complementary thymine counterpart.[9]

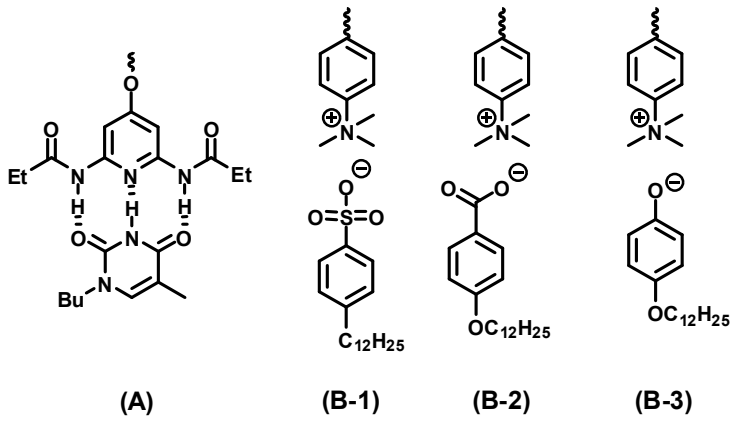


Figure 4.2 Self-assembly motifs used in this study: (A) three point hydrogen-bonded complex between 2,6-diaminopyridine and *N*-butylthymine, and (B) Coulombic self-assembly between the quaternary ammonium group and (B-1) sodium dodecyl sulfonate, (B-2) sodium stearate, and (B-3) sodium dodecyloxy phenolate.

The components for the Coulombic self-assembly consist of quaternary ammonium iodide which can be self-assembled with three different complementary recognition units **5**-**7** (Figures 4.2 and 4.3). The recognition units are based on the sodium salts of long alkyl chain functionalized sulfonic acid (sodium dodecyl sulfonate-SDS), carboxylic acid (sodium stearate-SS), and phenol (sodium dodecyloxy phenolate-SDP). The long alkyl chains enhance the solubility of these salts in nonpolar solvents such as $CHCl_3$ and CH_2Cl_2 in which all self-assembly experiments were carried out. The three different anionic recognition units were chosen to study the effect of the hydrogen bonding acceptors (oxygen atoms) on the anionic moieties. Each of the three anionic recognition units has a differing number of oxygen atoms, capable of disrupting the hydrogen bonding interactions between *N*-butylthymine and 2, 6-diaminopyridine.

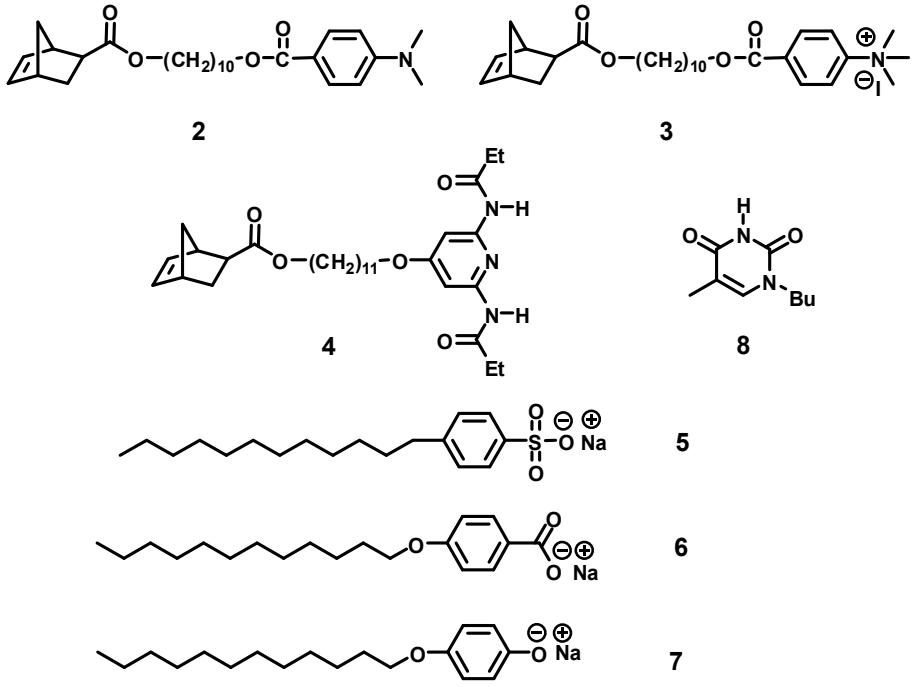
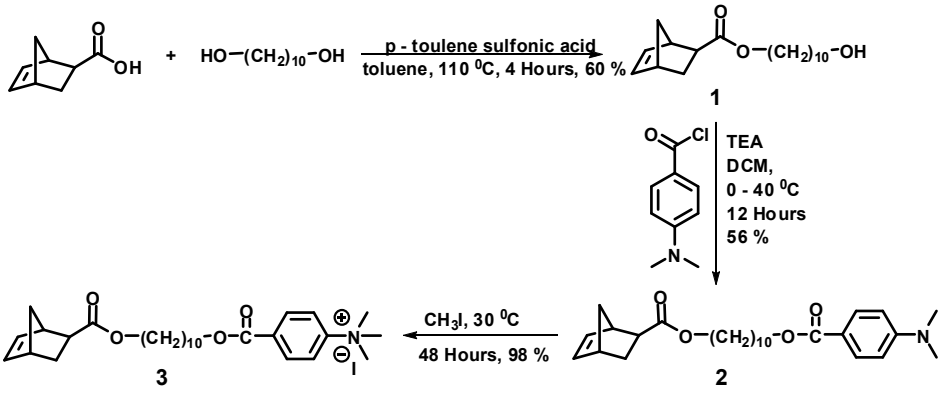


Figure 4.3 Monomers **2-4** and recognition units **5-8** used in this study.

4.4 Synthesis of monomers and recognition units

All monomers are derived from 100% isomerically pure *exo*-norbornene acid.[28,29] Monomer **3** was synthesized as outlined in Scheme 4.1. Esterification of *exo*-norbornene acid with an excess of 1,10-decanediol using *p*-toluene sulfonic acid as the catalyst in toluene gave the monoester alcohol **1**. Compound **1** was then esterified with 4-(dimethylamino) benzoyl chloride in CH_2Cl_2, to yield the tertiary amine monomer **2**.



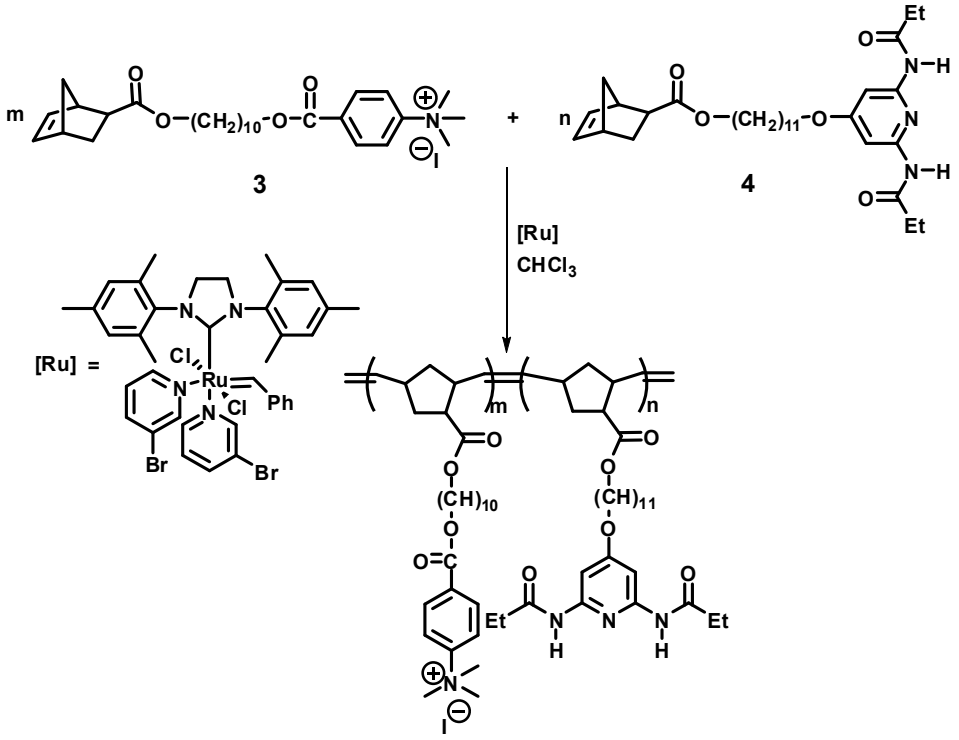
Scheme 4.1 Synthesis of monomer **3**.

Monomer **3** was then synthesized by quantitatively converting the tertiary amine group of monomer **2** to a quaternary ammonium group, which was achieved by reacting **2** with an excess of iodomethane at 30°C for 48 hours.[30] The quantitative quaternization of **2** was determined by ^{1}H NMR spectroscopy. Upon complete quaternization, the methyl signals showed a complete downfield shift from 3.00 ppm to 4.00 ppm. Furthermore, due to the strong negative inductive effect of the quaternary ammonium group, the aromatic signals also showed significant shifts from 6.63 ppm to 8.13 ppm and from 7.90 ppm to 8.28 ppm. Isolation of the analytically pure monomer **3** from monomer **2** was facile, as monomer **2** is a liquid and soluble in hexanes, whereas monomer **3** is a solid and insoluble in hexanes. As a result, filtration and repeated washings with ice-cold hexanes followed by prolonged drying under high vacuum yielded pure **3** as a pale yellow solid.

4.5 Homopolymerization studies

Although monomer **2** could be polymerized using Grubbs' second and third generation initiators, monomer **3** could only be polymerized using Grubbs' third generation initiator which has been reported to have high catalytic activity and functional group tolerance.[31] Quantitative conversions of monomer **3** could be achieved in less than five minutes at room temperature using $CHCl_3$ as the solvent as determined by ^{1}H NMR spectroscopy. **Poly-3** had limited solubility in solvents such as CH_2Cl_2, $CHCl_3$, and THF, but was completely soluble in strongly polar solvents such as DMF and DMSO. Once Grubbs' third generation initiator was found to polymerize monomer **3**, the homopolymerization was studied in detail. A series of homopolymerizations with monomer to initiator ratios (M/I ratios) ranging from 10:1 to 250:1 were carried. It was

found that molecular weights of the resulting polymers were independent of the M/I ratio used indicating an uncontrolled polymerization. For all M/I ratios studied, the M_n was in the range of 8,000-9,000 with the PDI ranging from 1.2 to 1.3 (GPC analysis of **Poly-3** were carried out using DMF as the solvent and poly(styrene)s as standards). To further probe the polymerization of **3**, the carbene signal was monitored during polymerization. Upon addition of **3** to the catalyst solution, complete disappearance of the uninitiated carbene signal at 19.09 ppm without any presence of either initiated or uninitiated carbene signals were observed confirming the uncontrolled nature of this polymerization.



Scheme 4.2 Random copolymerization of monomers **3** and **4** in chloroform at room temperature using Grubb's third generation initiator.

4.6 Copolymerization studies

Monomers **2** and **4** could be quantitatively copolymerized using Grubbs' third generation initiator in less than five minutes. All copolymers based on **2** and **4** with varying composition were soluble in non-polar solvents such as CH_2Cl_2 and $CHCl_3$.

Table 4.1 GPC data of unfunctionalized homo and copolymers. (a) Eluant: DMF. Polymer abbreviations are based on Scheme 4.3.

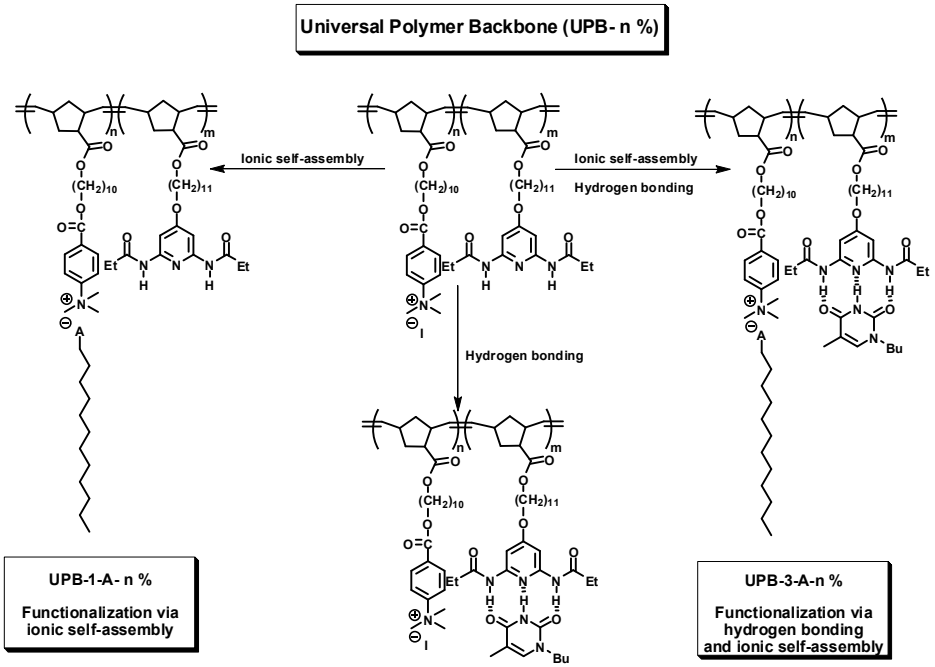
Entry	[M]/[I]	M_n (10^3)	M_w (10^3)	PDI
Poly-2	50	5.3	6.7	1.26
Poly-3	50	8.5	13.0	1.23
Poly-4[(a)]	50	10.4	13.0	1.25
UPB-10%	50	7.1	9.0	1.26
UPB-15%	50	8.0	9.7	1.22
UPB-20%	50	8.7	10.6	1.21
Control	50	63.0	97.5	1.54

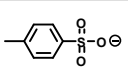
Similarly **3** and **4** could be copolymerized using Grubbs' third generation initiator to yield copolymers having both hydrogen bonding and charged sites. GPC analyses of the resulting copolymers shows unimodal curves with PDIs around 1.2 as listed in Table 4.1. However, the solubility of copolymers **3** and **4** was highly dependent upon the mole fraction of the charged monomer **3**. All copolymers having less than 20 mol% of monomer **3** were completely soluble in non polar solvents such as $CHCl_3$ and CH_2Cl_2. However, increasing the concentration of **3** above 20 mol% resulted in copolymers that phase separated in these solvents, but were completely soluble in polar solvents such as THF and DMF. Unfortunately, due to the competing nature of these solvents, they do not

allow for formation of strong hydrogen bonds between 2,6-diaminopyridine and *N*-butylthymine, thereby eliminating these solvents for our self-assembly studies.

4.7 Noncovalent functionalizations

The copolymers thus synthesized have both hydrogen bonding and ionic sites along the polymer backbone which after multi-functionalization can yield a family of functionally varied copolymers from a single polymer backbone.[7,8] Functionalization of the resulting copolymers using noncovalent interactions as well as investigation into the orthogonal character of all functionalization steps is the basis of this work. Therefore the subsequent step was to study the noncovalent functionalizations of all copolymers *via* hydrogen bonding and/or Coulombic self-assembly as depicted in Scheme 4.3.



UPB	UPB-1-SDS UPB-3-SDS	UPB-1-SS UPB-3-SS	UPB-3-SDP UPB-3-SDP	UPB-2
$A^{\ominus}$				None

Scheme 4.3 Functionalization strategies of the random copolymers. Nomenclature: n% denotes the percentage of monomer **3**; **UPB-1** indicates functionalization through Coulombic self-assembly; **UPB-2** indicates functionalization through hydrogen bonding; **UPB-3** indicates complete functionalization through both interactions; SDS, SDP and SS represent the anionic recognition units **5**, **6** and **7** respectively used for ionic self-assembly. Hence the polymer abbreviation **UPB-1-SDS-20%** would indicate a copolymer of **4** and **3** (20 mol%) which is functionalized by ionic self-assembly using **5**.

4.8 Monomer studies

4.8.1 *Qualitative analysis: Hydrogen bonding interactions*

One of the aims of this work was to determine if the hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine were affected by the presence of ionic charges and subsequent Coulombic self-assembly. To investigate this, ^{1}H NMR spectroscopy was used to monitor the chemical shifts of the amide protons of 2,6-diaminopyridine and the chemical shifts of the imide proton of *N*-butylthymine during the hydrogen bond formation both in the presence and in the absence of ionic charges and Coulombic self-assembly. For these qualitative analyses, the copolymers based on **4** and **3** having equimolar amounts of the recognition units, could not be used as they were sparingly soluble in $CHCl_3$. Hence these qualitative analyses were carried out using monomers **3** and **4**, which were completely soluble in equimolar ratios in $CHCl_3$, thus permitting to accurately and reliably study the effect of ionic charges and self-assembly on the 2,6-diaminopyridine-*N*-butylthymine complex formation. Furthermore, to study if the sequence of the hydrogen bonding and ionic self-assemblies would have any effect on the complex formation of 2,6-diaminopyridine and *N*-butylthymine, the multiple self-assembly experiments were carried out in three distinct ways:

(A) Hydrogen bonding followed by Coulombic self-assembly.

This investigation was carried out to study the affect of the ionic charges and Coulombic self-assembly on the hydrogen bonded complex between **4** and **8**. In this experiment, **4** and **8** were first self-assembled to form the corresponding hydrogen bonded complex, after which an equimolar amount of **3** was added to the complex. It was found that the amide and the imide protons of the hydrogen bonded complex did not undergo any changes in their chemical shifts, indicating that the presence of ionic charges did not interfere in the hydrogen bonding interactions of **4** and **8**. Further, the effect of Coulombic self-assembly was investigated and monomer **3** in the above experiment was self-assembled with **5**, **6** and **7** individually. In each case it was found that the proton shifts of the hydrogen bonded complex were not affected upon the Coulombic self-assembly. The NMR data is listed in Table 4.2 and clearly establishes that the hydrogen bonding between **4** and **8** is not disrupted by the presence of **3** and its subsequent Coulombic self-assembly.

Table 4.2 Amide and imide proton chemical shifts in ppm measured by ^{1}H NMR spectroscopy of the hydrogen bonded complex between **4** and **8**, using three different functionalization routines: (A) hydrogen bonding followed by Coulombic self-assembly, (B) Coulombic self-assembly followed by hydrogen bonding, and (C) one-step multi-functionalization.

(A) Hydrogen bonding followed by Coulombic self-assembly			(B) Coulombic self-assembly followed by hydrogen bonding		
Entry	**Chemical Shift (ppm)**		**Entry**	**Chemical Shift (ppm)**	
	Amide protons of 4	**Imide protons of 8**		**Amide protons of 4**	**Imide protons of 8**
4	7.57	N A	**3** + **5** + **4** + **8**	9.16	10.54
8	N A	8.02	**3** + **6** + **4** + **8**	9.11	10.60
4 + **8**	9.21	10.64	**3** + **7** + **4** + **8**	9.18	10.60
4 + **8** + **3**	9.17	10.54	**(C) Simultaneous multi-functionalization**		
4 + **8** + **3** + **5**	9.21	10.56	**(4+3)** + **(8+5)**	9.11	10.63
4 + **8** + **3** + **6**	9.15	10.61	**(4+3)** + **(8+6)**	9.13	10.62
4 + **8** + **3** + **7**	9.17	10.61	**(4+3)** + **(8+7)**	9.14	10.56

(B) Coulombic self-assembly followed by hydrogen bonding.

In this functionalization mode, the Coulombic self-assembly was followed by hydrogen bonding. Monomer **3** was self-assembled with **5**, **6**, or **7** individually to form three distinct ionic complexes. Subsequently an equimolar amount of **4** was added to the ionic complexes. It was found that the amide protons of **4** did not undergo any changes in their chemical shifts. Furthermore, when **4** was self-assembled with an equimolar amount of **8**, the amide and the imide protons shifts of the complex of **4** and **8** were not affected by the Coulombic self-assembled complexes. These results clearly illustrate that the route of functionalization does not affect the hydrogen bonding between **4** and **8**.

(C) Simultaneous multi-functionalizations.

To investigate if both ionic self-assembly and hydrogen bonding can be carried together simultaneously, simultaneous multi-functionalization experiments were carried out. Monomers **3** and **4** were simultaneously self-assembled using ionic self-assembly and hydrogen bonding interactions respectively. Here again it was found that the amide and the imide protons shifts of the complex of **4** and **8** were independent, i.e. the hydrogen bonding interaction was not affected by the Coulombic self-assembly and was independent of the anionic recognition units **5**, **6**, and **7**.

4.8.2 *Qualitative analysis: Coulombic self-assembly*

It was not possible to characterize the Coulombic self-assembly via NMR spectroscopy since it involves only the exchange of the counter anions. No visible shifts of the chemical shifts of the protons (methyl protons attached to the quaternary nitrogen atom, aromatic nucleus and the methylene carbon atom adjacent to the aromatic nucleus) were detected. Also no significant shifts in the ^{13}C spectra were observed upon coulombic self-assembly, preventing the use of ^{13}C NMR for qualitative information.

Hence the Coulombic self-assembly between **3** with **5**, **6**, and **7** was studied by using infrared spectroscopy by monitoring the distinct absorption bands around 3000 cm^{-1} and 1500 cm^{-1} ($-N^{+}(CH_3)_3$ group), 1245 cm^{-1} (sulfonate group), around 1560 cm^{-1} (carboxylate group) and around 1235 cm^{-1} (phenate group).[32-34] The IR spectra can be found in the appendix to this chapter. First, the changes of the IR stretches during the hydrogen bonding self-assembly were investigated. Upon self-assembly of **4** and **8**, the free amide vibration band of **4** at 3320 cm^{-1} was completely shifted to 3280 cm^{-1}, whereas the free imide vibration band of **8** was completely shifted to 3210 cm^{-1}.[35] Next the effect of **5**, **6** and **7** which have hydrogen bond acceptor oxygen moieties on **4** was studied to see if there was any hydrogen bonding interactions. The vibrational frequencies of the amide group of **4** in the presence of **5** was monitored. No shifting of the amide frequency at 3320 cm^{-1} as well as the sulfonate frequency at 1245 cm^{-1} was detected indicating the absence of any interactions between the sulfonate groups and the amide groups of **4**. Furthermore, when **4** and **8** were self-assembled in the presence of **5**, the distinctive shifts of both the amide and the imide frequencies of **4** and **8** were observed without any shifting of the sulfonate group at 1245 cm^{-1}. Next **5** was self-assembled with **3** and it was found that the positions of the amide band of **4**, the imide band of **8** and the sulfonate band of **5** were not altered. Furthermore the same experiments using **6** and **7** were carried out and similar results were observed indicating the absence of hydrogen bonding interactions between the amide groups of **4** with the carboxylate and the phenate groups, respectively. The detailed IR shifts values are tabulated in Table 4.3.

Table 4.3 Wavenumbers of (1) N-H stretch of **4** and **5**, (2) counter anion $\mathbf{A}^{-}$.
(*a*) sulfonate group, (*b*) carboxylate group, (*c*) phenate group.

Entry	Wavenumber (cm^{-1})			Entry	Wavenumber (cm^{-}		
	Amid	Imide	A^-		Amid	Imide	A^-
4 + **5**	3320	NA	1245	**4** + **8** + **6**	328	3210	156
4 + **8** + **5**	3280	3210	1245	**4** + **7**	3320	NA	123
4 + **8** + **5**	3280	3210	1245	**4** + **8** + **7**	328	3210	123
4 + **6**	3320	NA	1560	**4** + **8** + **7**	328	3210	123
4 + **8** + **6**	3280	3210	1560				

4.8.3 *Quantitative analysis: Hydrogen bonding interactions*

After performing the qualitative analysis, detailed quantitative analyses were carried out by measuring the K_a values of 2, 6-diaminopyridine and *N*-butylthymine in the presence and absence of the charged ionic species. First preliminary studies using monomer **4** and its complimentary recognition unit **8** were carried out. Using ^{1}H NMR spectroscopy titration experiments, the K_a of the hydrogen bonded complex between **4** and **8** was determined to be 900 M^{-1} which is comparable to published values.[35,9] Next it was investigated whether the anionic recognition species **5**, **6**, or **7** would interfere in the hydrogen bonded complex formation between **4** and **8**. Therefore monomer **4** was titrated against **8** in the presence of equimolar concentrations of **5**, **6**, or **7**. In all cases it was found that the K_a values were identical to those for the hydrogen bonding between **4** and **8** without the presence of any salt, which indicates that presence of anionic functional groups such as sulfonate, carboxylate and phenolate does not appreciably interfere in the

hydrogen bonding interactions between **4** and **8**. Figure 4.4 and Table 4.4 outline these results.

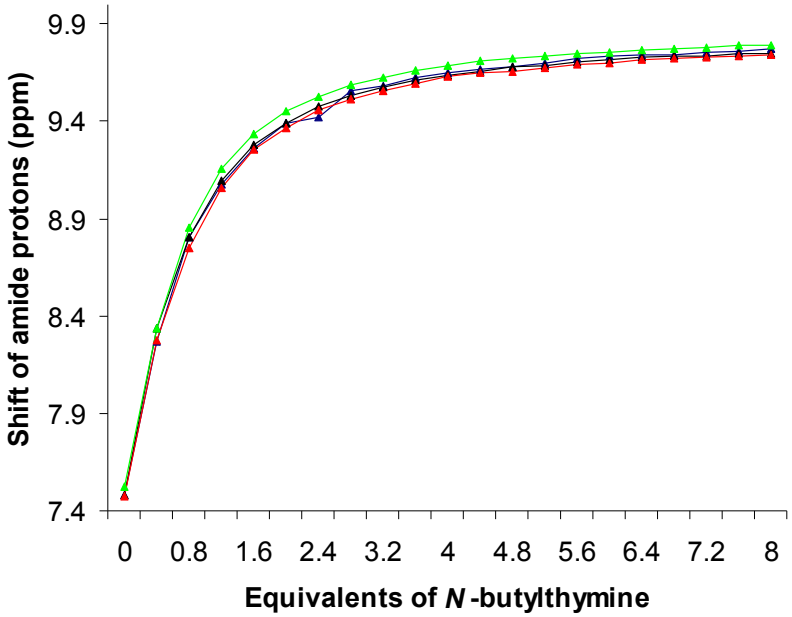


Figure 4.4 ^{1}H NMR spectroscopy titration curves for monomer **4** (▲), monomer **4** + **5** (▲), monomer **4** + **6** (▲) and monomer **4** + **7** (▲) with *N*-butylthymine **8**. The solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature in $CHCl_3$.

Table 4.4 K_a values for the self-assembly via hydrogen bonding of monomer **4** before and after Coulombic self-assembly. (1) Errors for all K_a measurements ranged from 10 to 15%.

Entry	K_a value[(1)]	Entry	K_a value[(1)]
4 + **8**	900 M^{-1}	**4** + **7** + **8**	895 M^{-1}
4 + **3** + **8**	920 M^{-1}	**4** + **3** + **5** + **8**	945 M^{-1}
4 + **5** + **8**	885 M^{-1}	**4** + **3** + **6** + **8**	822 M^{-1}
4 + **6** + **8**	922 M^{-1}	**4** + **3** + **7** + **8**	1000 M^{-1}

To study the effect of the cationic quaternary ammonium salt group on the hydrogen bonding interactions, **4** was titrated against **8** in the presence of an equimolar

concentration of **3**. No changes in the K_a values were observed, indicating that the presence of the quaternary ammonium salt does not interfere with the hydrogen bonding interactions. Furthermore, the quantitative effect of ionic self-assembly on hydrogen bonding interactions was investigated. Monomer **3** in the above experiment was then self-assembled with **5**, **6**, or **7** individually, and subsequently ^{1}H NMR titration studies were carried out. In each case it was observed that the K_a values (Table 4.4) did not show any significant deviations from K_a values for the complex of **4** and **8** in the absence of any charged species. This clearly establishes that the hydrogen bonding between **4** and **8** is not disrupted by the presence of **3** and its subsequent Coulombic self-assembly.

These preliminary monomer studies indicate that the presence of anions such as sulfonate **5**, carboxylate **6**, and phenolate **7** containing three, two and one oxygen atoms respectively that are able to act as potential hydrogen bond acceptors do not disrupt the hydrogen bond complex formation between **4** and **8**. Furthermore, when these anions are complexed with **3**, the presence of the ionic complex does not cause any disruption of the hydrogen bonded complex formation of **4** and **8**. After these preliminary experiments, the self-assembly of all copolymers by using either hydrogen bonding or ionic self-assembly as well as the stepwise multi-functionalization beginning with the ionic self-assembly followed by hydrogen bonding as depicted in Scheme 4.3, was carried out.

4.9 Polymer studies

4.9.1 *Quantitative analysis: Hydrogen bonding interactions*

All copolymers were easily self-assembled via hydrogen bonding by simply stirring the polymer solution in CH_2Cl_2 with the calculated amounts of **8** (based on the 2,6-diaminopyridine moieties along the polymers), followed by the removal of the

solvent under reduced pressure. The K_a values for all copolymers measured by ^{1}H NMR spectroscopy titration experiments were found to decrease from 900 M^{-1} to around 500 M^{-1}. This result was expected since similar decreases in the K_a values have been previously reported upon polymerization of hydrogen bonding monomers based on 2,6-diaminopyridines.[9,36]

To study the effect of copolymer composition on the K_a values, three different copolymers were synthesized having three different ratios of monomer **3** to monomer **4** (10:90, 15:85, 20:80 mol%). The K_a values (Table 4.5 and Figure 4.5) of these three different copolymers were identical within the experimental error indicating that the copolymer composition has no effect on the K_a values. Furthermore, a control copolymer using monomers **2** and **4** (equimolar amounts of **2** and **4**, [M]/[I] = 50) was synthesized. This control copolymer does not contain any charged species along the polymer backbone and allowed for easy comparison of the effect of the ionic charges. Again, it was found that the K_a value (K_a = 520 M^{-1}) of the control copolymer was identical, within the error range, to those copolymers based on monomers **3** and **4** indicating that the presence of the ionic sites along the polymer does not interfere with the hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine.

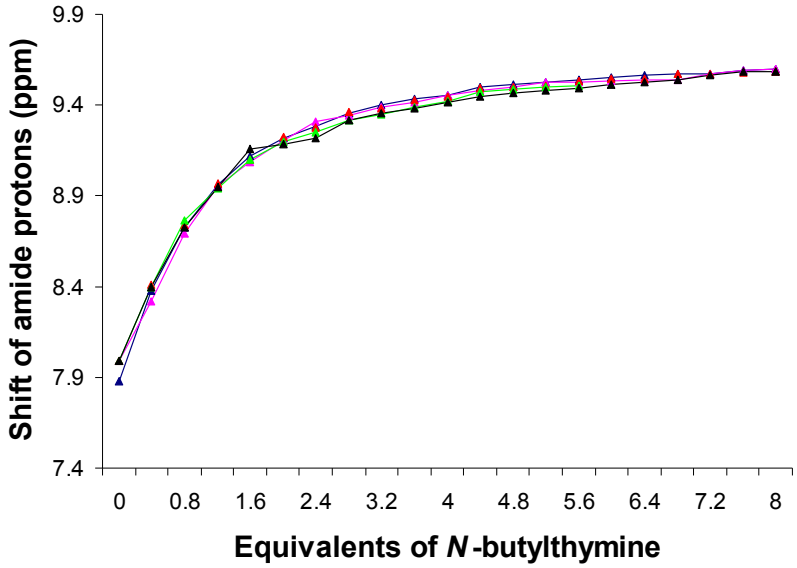


Figure 4.5 ^{1}H NMR spectroscopy titration curves for **Poly-4** (▲), **control polymer** (▲), **UPB-10%** (▲), **UPB-15%** (▲) and **UPB-20%** (▲) with *N*-butylthymine. The solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature in $CHCl_3$.

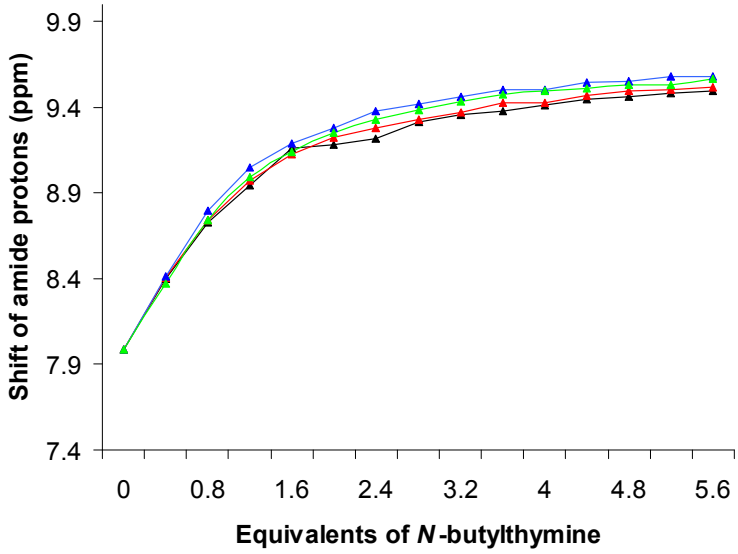


Figure 4.6 ^{1}H NMR spectroscopy titration curves for **UPB-20%** (▲), **UPB-1-SDS-20%** (▲), **UPB-1-SDP-20%** (▲) and **UPB-1-SS-20%** (▲) with *N*-butylthymine. The solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature in $CHCl_3$.

Table 4.5 K_a values for the self-assembly *via* hydrogen bonding of copolymers based on monomers **3** and **4** before and after Coulombic self-assembly. Polymer abbreviations are based on Scheme 4.3. (1) Errors for all K_a measurements ranged from 10 to 15%.

Entry	K_a value[(1)]	Entry	K_a value[(1)]
UPB-10%	505 M^{-1}	**UPB-1-SS-10%**	650 M^{-1}
UPB-15%	415 M^{-1}	**UPB-1-SS-15%**	550 M^{-1}
UPB-20%	555 M^{-1}	**UPB-1-SS-20%**	560 M^{-1}
UPB-1-SDS-	450 M^{-1}	**UPB-1-SDP-**	525 M^{-1}
UPB-1-SDS-	535 M^{-1}	**UPB-1-SDP-**	620 M^{-1}
UPB-1-SDS-	505 M^{-1}	**UPB-1-SDP-**	660 M^{-1}

4.9.2 *Coulombic self-assembly*

Functionalization of the quaternary ammonium salt was carried out by dissolving the copolymers in dry CH_2Cl_2, and then adding a calculated amount of the appropriate recognition unit **5**, **6**, or **7**. The solution was stirred for 30 minutes after which the solvent was evaporated under reduced pressure.

4.9.3 *Step-wise multi-functionalizations*

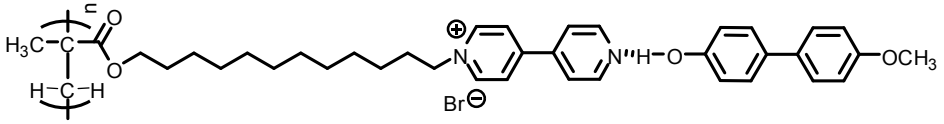
After establishing that a) the Coulombic self-assembly of all copolymers can be carried out without interference of the hydrogen bonding recognition motifs and the hydrogen-bonding based functionalization of the copolymers, b) the strength of the hydrogen bonding interaction is independent of the copolymers used, c) the strength of the hydrogen bonding interaction is independent of the Coulombic recognition pair employed, studies towards the ultimate goal of multi-functionalization of polymer scaffolds were carried out. In particular, we investigated the hydrogen bonding strength *via* ^{1}H NMR spectroscopy titration experiments of copolymers that were first functionalized *via* Coulombic self-assembly. All three complementary recognition units

5, **6**, and **7** were used for these studies. As shown in Figure 4.6 and Table 4.5, similar K_a values for the hydrogen bonding titration experiments for all copolymers self-assembled with **5**, **6**, and **7** were observed. Furthermore, the K_a values were also independent of the composition of the copolymers functionalized by Coulombic self-assembly. These results clearly demonstrate that Coulombic self-assembly does not interfere with the hydrogen bonding functionalization, i.e. both recognition motifs are orthogonal to each other.

4.10 Summary and future outlook

In this chapter, random copolymers possessing both hydrogen bonding and charged ionic recognition sites *via* ROMP have been synthesized. The hydrogen bonding recognition system consisted of substituted 2,6-diaminopyridine and *N*-butylthymine, whereas the Coulombic self-assembly system is based on a quaternary ammonium salt and sodium salts of long alkyl chain sulfonic acid, stearic acid, and phenol. The effect of copolymerization, copolymer composition, and lastly Coulombic self-assembly on the noncovalent functionalization via hydrogen bonding was studied in detail. None of these variables had any substantial impact on the stability of the hydrogen bonded complexes. Since the hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine are highly sensitive to the solvent medium used, the multi-functionalizations were studied only in solvents such as chloroform or methylene chloride which offer superior solubility and do not disturb the hydrogen bonding interactions. Clearly the Coulombic interactions are also strongly solvent dependent and all results described in this manuscript are only valid for the solvent systems studied. Nevertheless, these results demonstrate that the hydrogen bonding interactions are

orthogonal to the Coulombic interactions. Therefore, combining a functional group tolerant polymerization route with noncovalent functionalization techniques, allows for the fast synthesis of highly functionalized materials. Using noncovalent interactions such as hydrogen bonding and ionic self-assembly, allows for the synthesis of a large variety of functionally varied polymers which widely differ in their physical and chemical properties from a single polymer backbone by simply altering the functionalization strategy. Such a strategy will be important in the synthesis of multi-functional materials for emerging advanced applications as reported by Bazuin.



SSLCP-A

Figure 4.9 Example of SSCLCP based on hydrogen bonding and Coulombic interactions and hydrogen bonding studied by Bazuin and co-workers.

Bazuin and co-workers reported the application of multiple noncovalent interactions in side-chain supramolecular polymers to form functional materials such as supramolecular side-chain liquid crystalline polymers (SSLCP).[10] They used poly(pyridylpyridinium dodecyl methacrylate) bromide with terminal pyridyl groups functionalized side-chains which acted as hydrogen bond acceptors, furthermore the pyridyl groups were in close proximity to an ion pair as the polymeric scaffold to anchor a series of phenolic mesogens to the scaffold by using single point hydrogen bonding interactions (Figure 4.9, SSLCP-A). They showed that the hydrogen bond complexation of the mesogens on to the polymer scaffold is successful, leading to formation of SSLCP exhibiting well-defined thermotropic LC characteristics. The hydrogen bonding between

the scaffold and the phenol-functionalized mesogens took place selectively and completely despite the presence of potentially interfering Coulombic groups. The presence of the Coulombic groups results in relatively high glass-transition temperatures of around 80°C in the presence of the lengthy side-chains, whereas the mesogen that was created by the hydrogen bonding complex formation promotes liquid crystalline character. Such a successful example of multi-functional material with important commercial properties demonstrates the potential of using side chain multi-functionalized polymers for advanced applications.

4.11 Experimental section

General

All reagents were purchased from Acros Organics, Aldrich, or Strem Chemicals and used without further purification unless otherwise noted. Triethylamine, methylene chloride, and deuterated chloroform ($CDCl_3$) were distilled over calcium hydride. Grubbs' third generation initiator was synthesized as reported.[37] Monomer **4**,[28] *N*-butylthymine,[36] isomerically pure *exo*-norbornene acid,[28,29] and sodium 4-(dodecyloxy) phenolate (SDP)[38] were synthesized according to published procedures. Sodium benzene dodecylsulfonate (SDS) and sodium stearate (SS) were used as received.

Characterization procedure

As reported in Chapter three. IR analyses were performed on a Shimadzu IR spectrometer. The samples were dissolved in dry CH_2Cl_2 and cast as a thin film on a NaCl disc.

10-Hydroxydecyl *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (1)

Exo-bicyclo [2.2.1] hept-5-ene-2-carboxylic acid (5 g, 0.036 mol) and 1,10-decane diol (12.6 g, 0.072 mol) were suspended in anhydrous toluene (100 mL). A catalytic amount of *p*-toluene sulfonic acid (0.37 g, 0.002 mol) was added and the mixture was refluxed at 110˚C for four hours. After cooling and filtering off the excess diol, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluant: hexanes: EtOAc, 3/1, v/v), and dried to yield **1** as a colorless liquid (6.12 g, 57%). ^{1}H NMR ($CDCl_3$): δ = 6.01 (m, 2H, CH=CH), 3.97 (t, 2H, *J* = 6.70 Hz, -$COOCH_2$-), 3.49 (t, 2H, *J* = 6.70 Hz, -CH_2-OH), 2.92 (s, 1H, norbornene signal), 2.81 (s, 1H, norbornene signal), 2.75 (s, 1H, norbornene signal), 2.12 (m, H, norbornene signal), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67-1.55 (m, 4H, -$(CH_2)_2$-), 1.51-1.25 (m, 10H, -$(CH_2)_5$-). ^{13}C NMR ($CDCl_3$): δ = 176.5, 138.1, 135.8, 64.7, 62.7, 46.4, 46.7, 43.3, 41.7, 32.8, 30.4, 29.6, 29.5, 29.3, 28.8, 26.0, 25.9. HRMS (FAB+) [M+1] calcd for $C_{18}H_{31}O_3$: 295.22732, found: 295.22962. Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27; Found: C, 70.20; H, 10.49.

10-(4-(Dimethylamino)benzoyloxy)decyl *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (2)

Compound **1** (1.0 g, 0.003 mol) and triethylamine (1.71 g, 0.016 mol) were dissolved in anhydrous CH_2Cl_2 (100 mL) and cooled to 0˚C. Then, 4-dimethylamino benzoyl chloride (0.64 g, 0.003 mol) was added slowly to the stirred solution. After one hour, the temperature was allowed to rise to room temperature followed by reflux for twelve hours. The reaction mixture was then cooled to room temperature and washed with 1 N HCl (100 mL) followed by saturated $NaHCO_3$ solution (100 mL). The organic phase was then dried over anhydrous magnesium sulfate and the solvent was removed

under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluant: hexanes: EtOAc, 1/2, v/v), and dried to yield **2** as a colorless liquid (0.80 g, 60%). ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, 2H, *J* = 9.95 Hz, Ar), 6.63 (d, 2H, *J* = 9.95 Hz, Ar), 6.11 (m, 2H, CH=CH), 4.24 (t, 2H, *J* = 6.70 Hz, -CH_2-OCO-Ar), 4.08 (t, 2H, *J* = 6.72 Hz, -$COOCH_2$-), 3.02 (s, 6H, -$N(CH_3)_2$), 3.00 (s, 1H, norbornene signal), 2.88 (s, 1H, norbornene signal), 2.31 (t, 2H, *J* = 7.08 Hz, -CH_2-), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67-1.55 (m, 4H, -$(CH_2)_2$-), 1.51-1.25 (m, 10H, -$(CH_2)_5$-). ^{13}C NMR ($CDCl_3$): δ = 176.5, 167.2, 153.4, 138.2, 136.0, 131.4, 117.5, 110.8, 64.8, 64.8, 46.8, 46.5, 43.4, 41.8, 40.2, 30.5, 29.6, 29.5, 29.4, 29.1, 28.9, 26.3, 26.1. HRMS (FAB+) [M+1] calcd for $C_{27}H_{40}NO_4$: 442.295, found: 442.293. Anal. Calcd for $C_{27}H_{39}NO_4$: C, 73.43; H, 8.90; N, 3.17 Found: C, 73.47; H, 9.16; N, 3.39.

4-((10-(*Exo*-bicyclo[2.2.1]hept-5-enecarbonyloxy)decyloxy)carbonyl)-*N*,*N*,*N*-trimethylbenzenaminium iodide (3)

Compound **2** (1.74 g, 0.003 mol) was dissolved in excess iodomethane (5.5 g, 0.039 mol) and stirred at 30˚C for two days. The excess iodomethane was removed under reduced pressure to give the crude product as a yellow solid. The solid was suspended in ice-cold diethyl ether, stirred for 30 minutes, and filtered. Then, the product was washed repeatedly with ice-cold hexanes and dried to yield the pure product **3** (1.71 g, 98%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ = 8.28 (d, 2H, *J* = 9.95 Hz, Ar), 8.13 (d, 2H, *J* = 9.95 Hz, Ar), 6.10 (m, 2H, CH=CH), 4.24 (t, 2H, *J* = 6.70 Hz, -CH_2-OCO-Ar), 4.08 (t, 2H, *J* = 6.72 Hz, -$COOCH_2$-), 4.05 (s, 9H, -$N(CH_3)_3$), 3.03 (s, 1H, norbornene signal), 2.90 (s, 1H, norbornene signal), 2.31 (m, 2H, *J* = 7.08 Hz, -CH_2-), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67-1.55 (m, 4H, -

$(CH_2)_2$-), 1.51-1.25 (m, 10H, -$(CH_2)_5$-). ^{13}C NMR ($CDCl_3$): δ = 176.5, 164.7, 150.2, 138.2, 135.9, 133.0, 132.2, 120.9, 110.8, 66.2, 64.7, 62.1, 58.1, 46.8, 46.5, 43.4, 41.8, 40.3, 30.5, 29.6, 29.4, 28.8, 26.1. HRMS (FAB+) [M – I + 1] calcd for $C_{28}H_{42}NO_4$: 456.311, found: 456.311. Anal. Calcd for $C_{28}H_{42}INO_4$: C, 57.63; H, 7.25; N, 2.40 Found: C, 57.35; H, 7.25; N, 2.51.

Homopolymerizations

The homopolymerization of monomer **3** is described as a representative example: Monomer **3** (22.1 mg, 0.037 mmol) was dissolved in 0.5 mL of $CHCl_3$. A stock solution of Grubbs' third generation initiator was prepared in $CHCl_3$ and an amount of the stock solution equaling 6.7 mg (0.379 mmol) of the initiator was added to the monomer solution. The solution was stirred 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. The polymer was isolated and purified by precipitating from ice-cold methanol, and repeated washings with ice-cold methanol and hexanes, followed by prolonged drying at room temperature under high vacuum.

Poly-2. ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, 2H, *J* = 9.95 Hz, Ar), 6.63 (d, 2H, *J* = 9.95 Hz, Ar), 5.34-5.18 (m, 2H, CH=CH), 4.24 (br m, 2H, -CH_2-OCO-Ar), 4.01 (br m, 2H, -$COOCH_2$-), 3.02 (s, 6H, -$N(CH_3)_2$), 2.68 (br m, 2H), 2.48 (br m, 2H), 2.31 (), 2.02-1.91 (br m, 2H), 1.60 (br m, 5H), 1.41 (br m, 2H), 1.25 (br s, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 134-131, 120.0, 64.7, 50-49, 47.8, 43.2, 42.1, 41.3, 37.2, 36.4, 29.5, 28.9, 29.1, 25.5.

Poly-3. ^{1}H NMR (d_6-DMSO): δ = 8.16 (distorted d, 2H, Ar), 8.10 (distorted d, 2H, Ar), 5.33-5.17 (m, 2H, CH=CH), 4.24 (br m, 2H, -CH_2-OCO-Ar), 3.99 (br m, 2H, -$COOCH_2$-), 3.65 (br s, 9H, -$N(CH_3)_3$), 2.48 (br m, 2H), 2.31 (m, 2H), 2.02-1.91 (br m, 2H), 1.60 (br m, 2H), 1.48 - 1.26 (br m, 14H). ^{13}C NMR (d_6-DMSO): δ = 165.0, 151.1, 138.5, 136.3, 131.9, 122.0, 65.9, 64.6, 57.1, 46.6, 43.2, 30.5, 29.6, 29.4, 29.3, 28.7, 26.1.

Copolymerizations

Random copolymers of **3** and **4** were synthesized in a similar fashion as outlined above. The synthesis of **UPB-10%** is described as a representative example of random copolymerization of **3** and **4**: Monomer **3** (22.1 mg, 0.037 mmol) was dissolved in 0.5 mL of $CHCl_3$ to which a 0.5 mL solution of monomer **4** (200 mg, 0.38 mmol) was added. A stock solution of Grubbs' third generation initiator was prepared in $CHCl_3$, and an amount of the stock solution equaling 6.7 mg (0.379 mmol) of the initiator was added to the monomer solution. The solution was stirred, and the reaction was monitored by observing the olefinic signals of the monomers by ^{1}H NMR spectroscopy. Upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization. Purification of all polymers was performed by precipitating the polymers from ice-cold methanol and repeated washings with ice-cold methanol and ice-cold hexanes, followed by prolonged drying at room temperature under high vacuum.

UPB-10%. ^{1}H NMR (d_7-DMF): δ = 8.40 (br d, 2H, Ar), 8.21 (br d, 2H, Ar), 7.57 (s, 2H, pyridyl), 5.34-5.18 (m, 2H, CH=CH), 4.36 (t, 2H, J = 6.6 Hz,), 4.04 (m, 2H), 3.94 (s, 9H, -$N(CH_3)_3$), 2.48 (br m, 2H), 1.78 (br s, 2H), 1.61 (br s, 2H), 1.32-1.10 (br m, 2H), 1.08 (t, 6H, J = 7.7 Hz). ^{13}C NMR (d_6-DMF): δ = 173.2, 168.3, 164.9, 152.3, 151.2, 132-131, 121.9, 95.4, 68.2, 65.8, 64.3, 56.9, 37.2, 34.0, 26.0.

Self-assembly experiments

Hydrogen bonding:

The synthesis of **UPB-2-10%** is described as a representative example: **UPB-10%** (222 mg, 0.379 mmol based on the 2,6-diaminopyridine functional groups along the polymer backbone) was dissolved in 5 mL of CH_2Cl_2. Then, 69 mg (0.379 mmol) of *N*-butylthymine was added and the solution was stirred for 30 minutes. The solvent was evaporated, and the self-assembled polymer **UPB-2-10%** was dried under high vacuum.

Coulombic self-assembly:

The synthesis of **UPB-1-SDS-10%** is described as a representative example: **UPB-10%** (222 mg, 0.0379 mmol based on the quaternary ammonium iodide groups along the polymer backbone) was dissolved in 5 mL of CH_2Cl_2, then 13.2 mg (0.037 mmol) of compound **5** was added, and the reaction mixture was stirred for 30 minutes. The solution was dried under high vacuum to yield the self-assembled polymer **UPB-1-SDS-10%.**

Titration experiments:

Association constants (K_a) were measured by ^{1}H NMR spectroscopy titrations at room temperature of a 0.005 M solution of the copolymers (based on the hydrogen bonding moieties) in deuterated $CHCl_3$ with a 0.01 M solution of *N*-butylthymine. The chemical shifts of the amide protons for the 2,6-diaminopyridines were monitored during the titration. The data was evaluated by ChemEquili software to calculate the association constants.[39] All titrations were conducted in duplicate. The errors ranged from 10 to 15%.

4.12 References

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4. 13Appendix
List of IR spectroscopy graphs

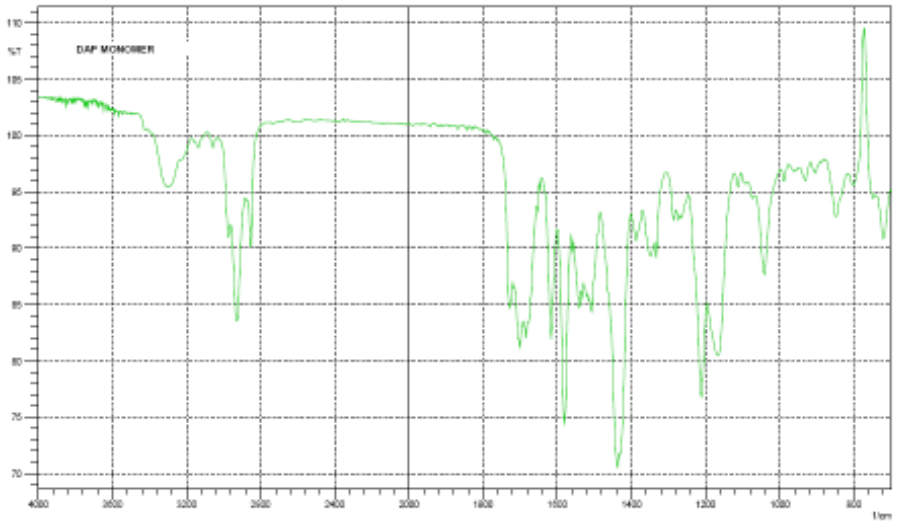


Figure 4.A IR spectrum of monomer **4**

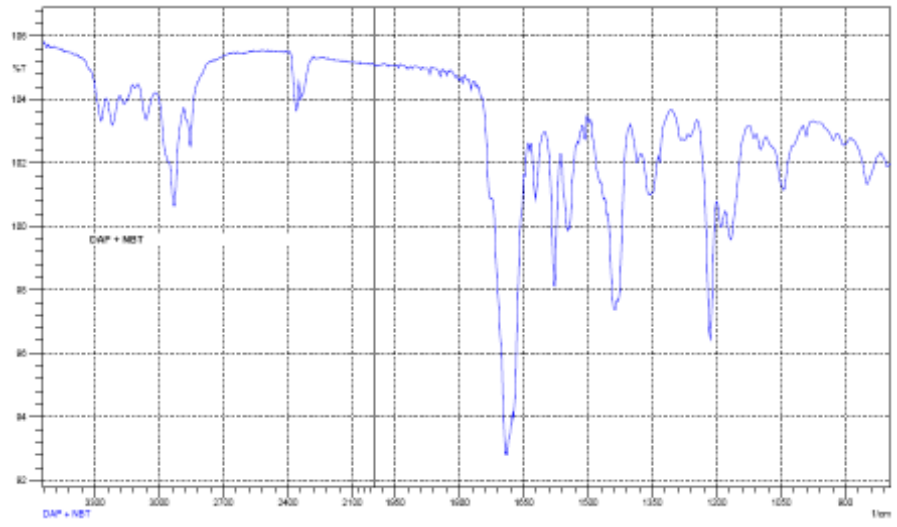


Figure 4.B IR spectrum of monomer **4 + 8** (1. Equivalent)

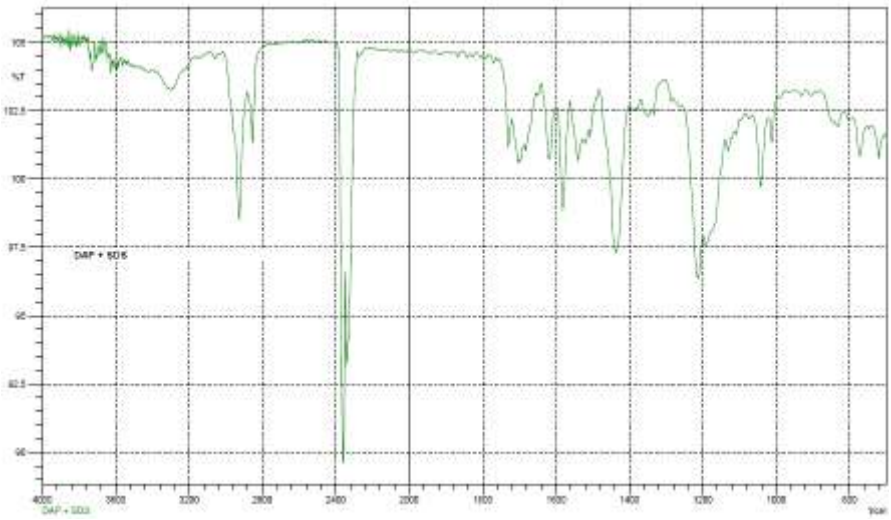


Figure 4.C IR spectrum of monomer **4** + **5** (1. Equivalent)

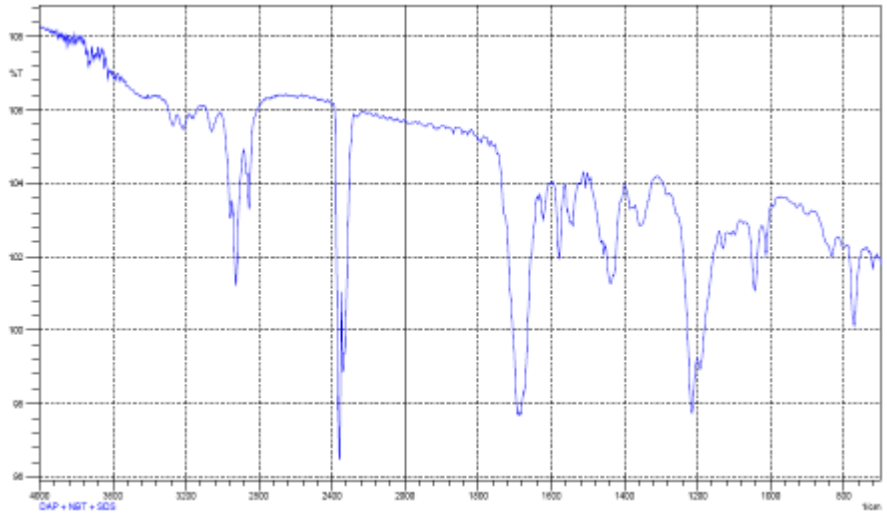


Figure 4.D IR spectrum of monomer **4** +**5** (1. Equivalent) +**8** (1. Equivalent)

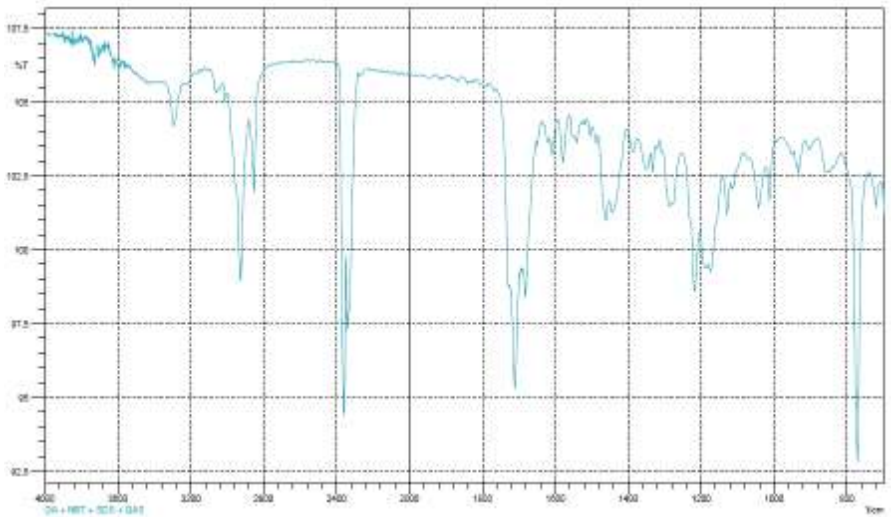


Figure 4.E IR spectrum of monomer **4 +8** (1. Equivalent) **+ 5** (1. Equivalent) + 3 (1. Equivalent)

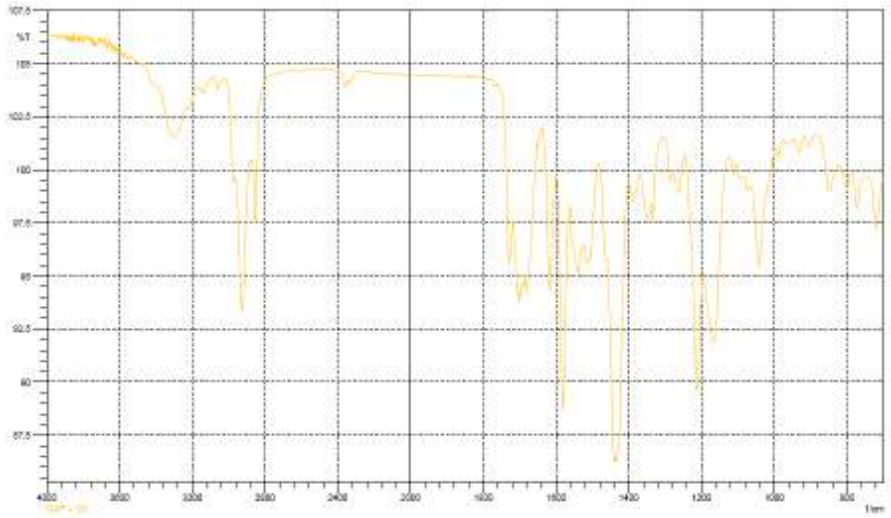


Figure 4.F IR spectrum of monomer **4 +6** (1. Equivalent)

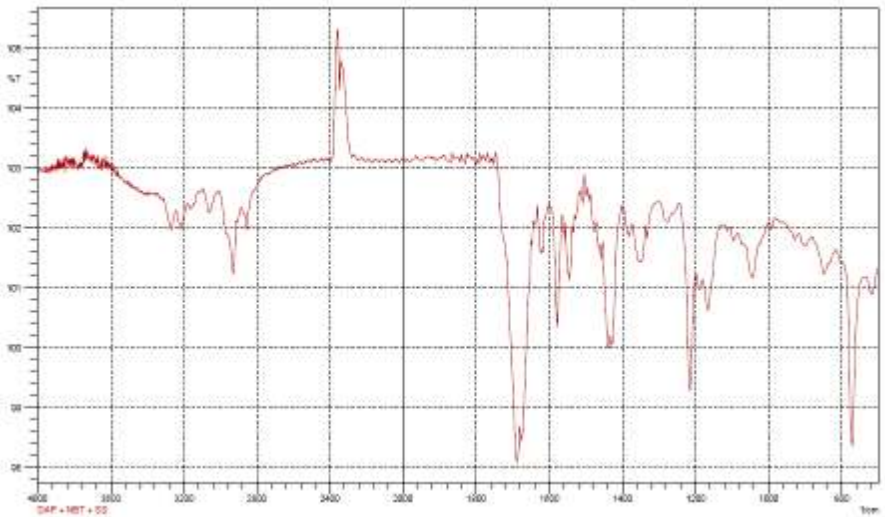


Figure 4.G IR spectrum of monomer **4** +**8** (1. Equivalent) + **6** (1. Equivalent)

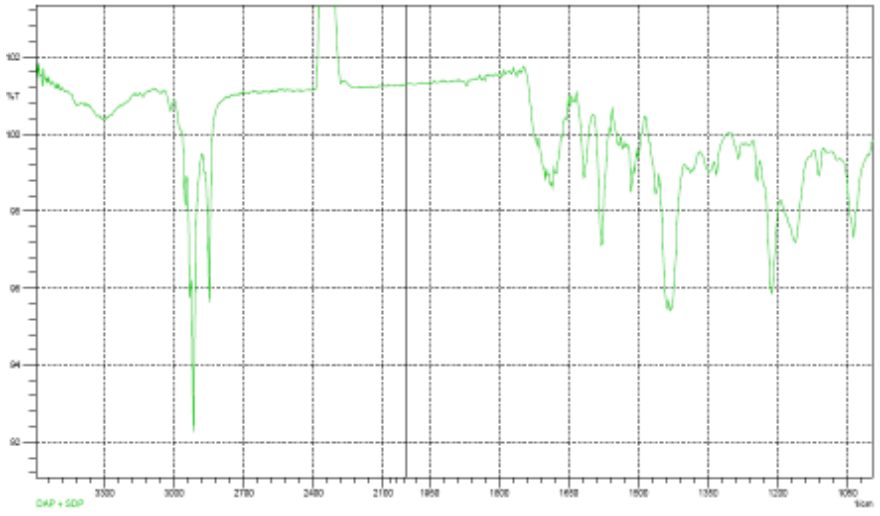


Figure 4.H IR spectrum of monomer **4** +**7** (1. Equivalent)

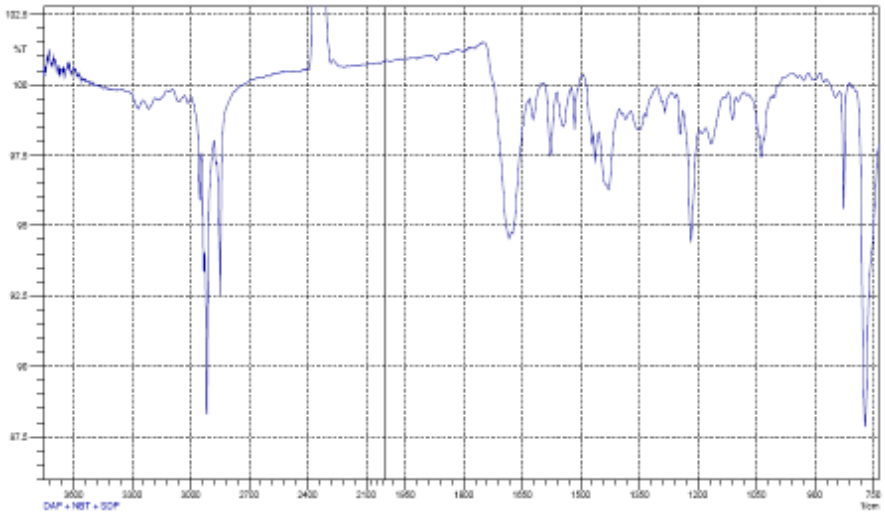


Figure 4.I IR spectrum of monomer **4** +**8** (1. Equivalent) + **7** (1. Equivalent)

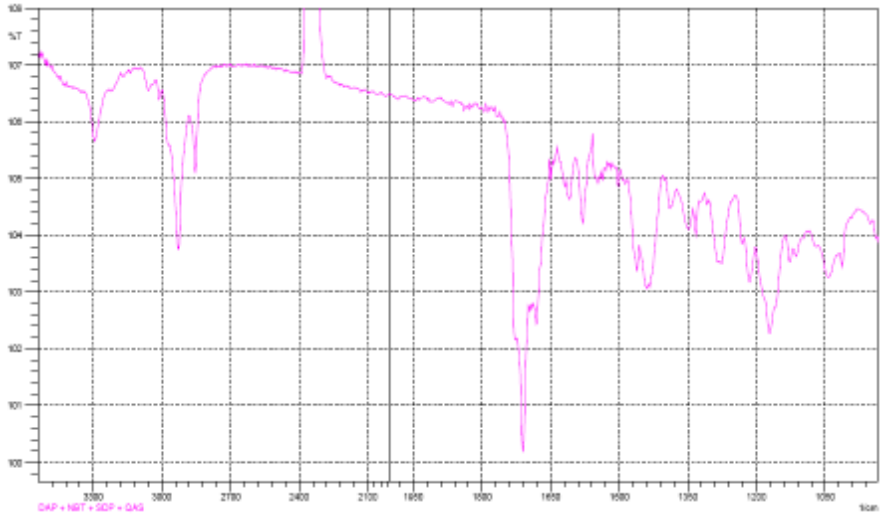


Figure 4.J IR spectrum of monomer **4** +**8** (1. Equivalent) + **7** (1. Equivalent) + **3** (1. Equivalent)

CHAPTER FIVE

Complementary Hydrogen Bonded Thermoreversible Polymer Networks Based on Cyanuric Acid

5.1 Abstract

Complementary hydrogen-bonded crosslinked polymer networks based on two distinct hydrogen bonding recognition motifs have been synthesized by using a combination of ROMP and hydrogen bonding interactions and were subsequently characterized in solution using rheometry. The hydrogen bonding recognition units were based either on three point cyanuric acid-2, 4-diaminotriazine or six point cyanuric acid-Hamilton wedge interactions. Through the addition of "ditopic crosslinking agents", the polymer scaffold, which was functionalized with cyanuric acid functional groups, was noncovalently crosslinked in solution through complementary inter-chain hydrogen bonding interactions. The extent of crosslinking could be controlled by varying the amount of the crosslinking agent added. These networks are thermally reversible and have highly tunable mechanical properties which are controlled by the molecular structure of the crosslinking agent. While addition of the Hamilton wedge crosslinking agent to the polymer solution led to high-viscosity fluids, the diaminotriazine crosslinking agent produced highly viscoelastic gels, in spite of the inherently weaker hydrogen bonding (three versus six point), due to higher connectivity between the crosslinking agent and polymer. The study shows that the micro-structure 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 micro-structure via the molecular architecture of the crosslinking agents.

5.2 Introduction

In Chapter two, the advantages of reversible polymer crosslinking techniques using noncovalent processes over conventional covalent crosslinking have been extensively discussed. In this chapter the use of hydrogen bonding interactions (specifically complementary hydrogen bonding interactions) to reversibly crosslink polymer scaffolds to yield a highly tunable, thermally reversible polymeric network will be discussed in detail. Furthermore, this chapter will focus on the specific advantages of using these interactions over dimerizing or self-complementary networks such that one can fine-tune network properties in solution by choosing the appropriate hydrogen bonding interaction, where the extent of crosslinking can simultaneously be tuned via the concentration of the crosslinking agent. 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. Furthermore, in Chapters one and two the specific advantages of using hydrogen bonding interactions for the polymer functionalization as well as for the synthesis of reversible crosslinked polymeric networks have been explained.[1,2]

In this study, this approach is extended by using a recognition motif attached to the polymer backbone that is able to form different hydrogen bonding motifs with crosslinking agents. Our hypothesis is that such a system will allow to tailor the materials properties in solution, in particular the degree of crosslinking 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.

5.3 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 5.1). 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 approximately 10^6 M^{-1} in chloroform.[8,13-15,6] This interaction has been used before in side-chain supramolecular polymers for side-chain functionalization.[13,6] 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.[16-19]

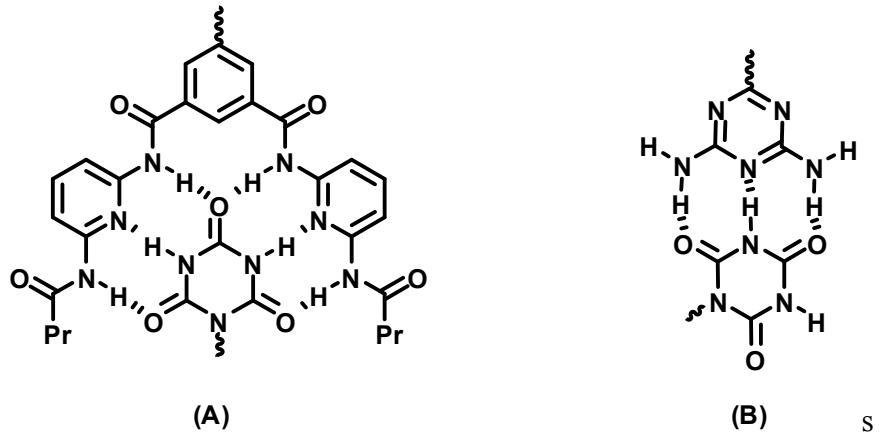


Figure 5.1 Self-assembly recognition pairs employed in this study: (A) six point hydrogen bonded complex between the Hamilton wedge receptor and cyanuric acid, (B) three point hydrogen bonded complex between 2,4-diaminotriazine and cyanuric acid.

The cyanuric acid moieties are anchored covalently onto a poly(norbornene) backbone by copolymerizing monomer **1** and the cyanuric acid containing monomer **2** using ROMP. The non-functionalized monomer **1** serves as a diluent for the cyanuric acid units and increases solubility of all copolymers in non-polar solvents.[6] Hydrogen bonded crosslinking was carried by employing either ditopic 2,4-diaminotriazine (crosslinking agent **3**) or ditopic Hamilton wedge receptors (crosslinking agent **4**). All crosslinking events as well as all characterizations of the resulting crosslinked polymer networks were carried out in 1-chloronaphthalene which is a non-competitive, high boiling solvent in which all copolymers are highly soluble. All monomers and crosslinking agents are shown in Figure 5.2. Monotopic agents **5** and **6** were used as model compounds to study the hydrogen bonding self-assembly.

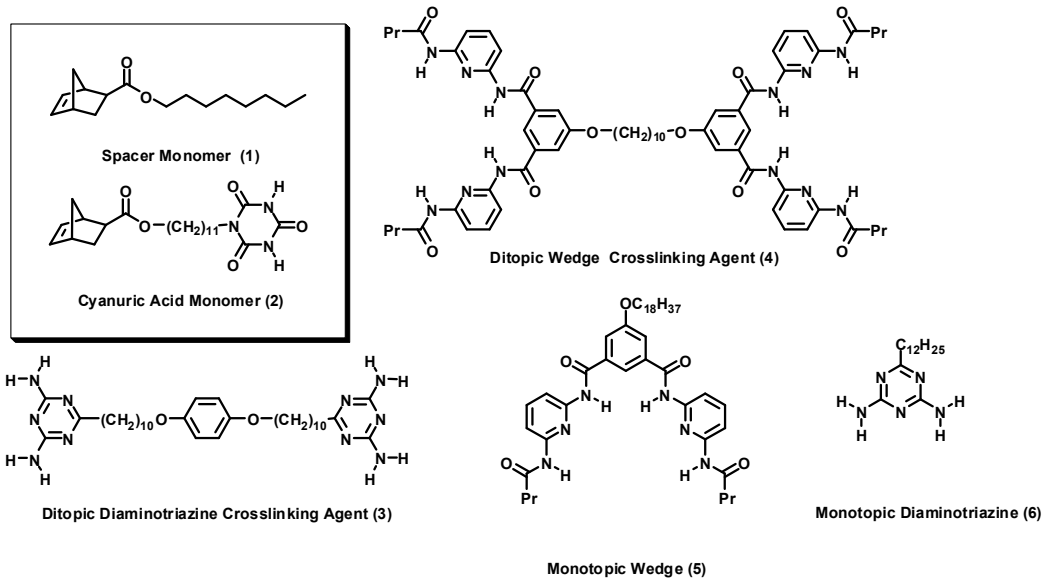
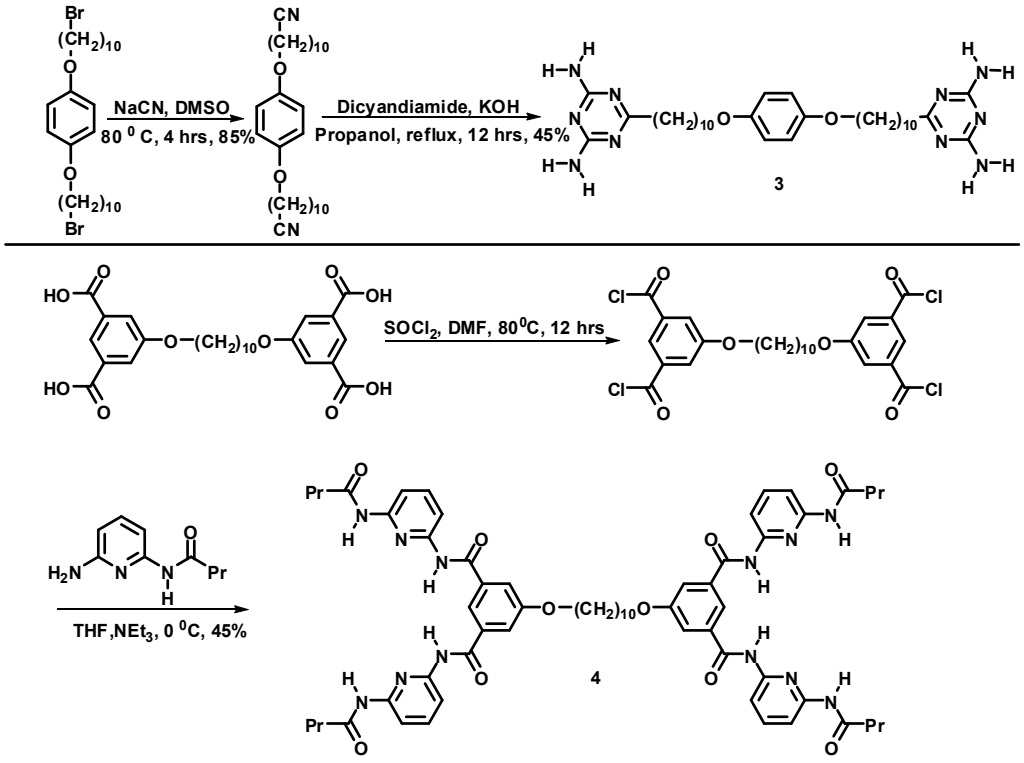


Figure 5.2 Monomers **1** and **2**, ditopic crosslinking agents **3** and **4** and monotopic functionalizing agents **5** and **6** utilized in this study.

5.4 Synthesis of crosslinking agents

Monomers **1** and **2** were synthesized according to literature procedures.[13,6] The ditopic diaminotriazine crosslinking agent **3** was synthesized from 1,4-bis(10-bromodecyloxy)benzene in two steps as outlined in Scheme 5.1. 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 di-nitrile was then treated with dicyandiamide in propanol in the presence of KOH to give **3** which was purified by repeated crystallizations from ethanol.[18]

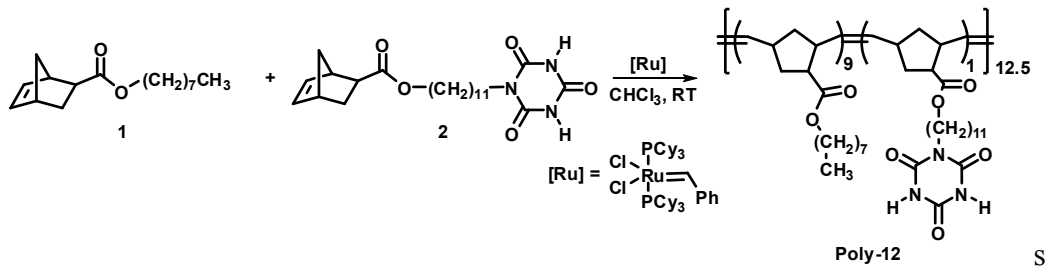


Scheme 5.1 Synthesis of ditopic 2,4-diaminotriazine crosslinking agent **3** and ditopic Hamilton wedge crosslinking agent **4**.

Crosslinking agent **4** was also obtained in two steps. First, the tetra-acid was converted to its corresponding acid chloride derivative by heating it to reflux in a large excess of thionyl chloride. After 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 twelve hours, the solvent was removed under reduced pressure and the residue suspended in ethyl acetate and filtered. Crosslinking 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 washings with ethyl acetate to remove the excess amine.

5.5 Copolymerization studies

We have previously reported the detailed polymerization behaviors of monomers **1** and **2**.[13,6] Both monomers can be copolymerized in a statistical manner via ROMP in chloroform at room temperature using Grubbs' first generation initiator (Scheme 5.2). We obtained complete monomer conversion within three hours. 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 5.1 lists the gel-permeation chromatography characterization of these polymers.



Scheme 5.2 Synthesis of **Poly-12** via ROMP using Grubbs' first generation initiator.

Table 5.1 GPC data of **Poly-12** using THF as the eluent. Polymer molecular structure is described in Scheme 5.2.

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

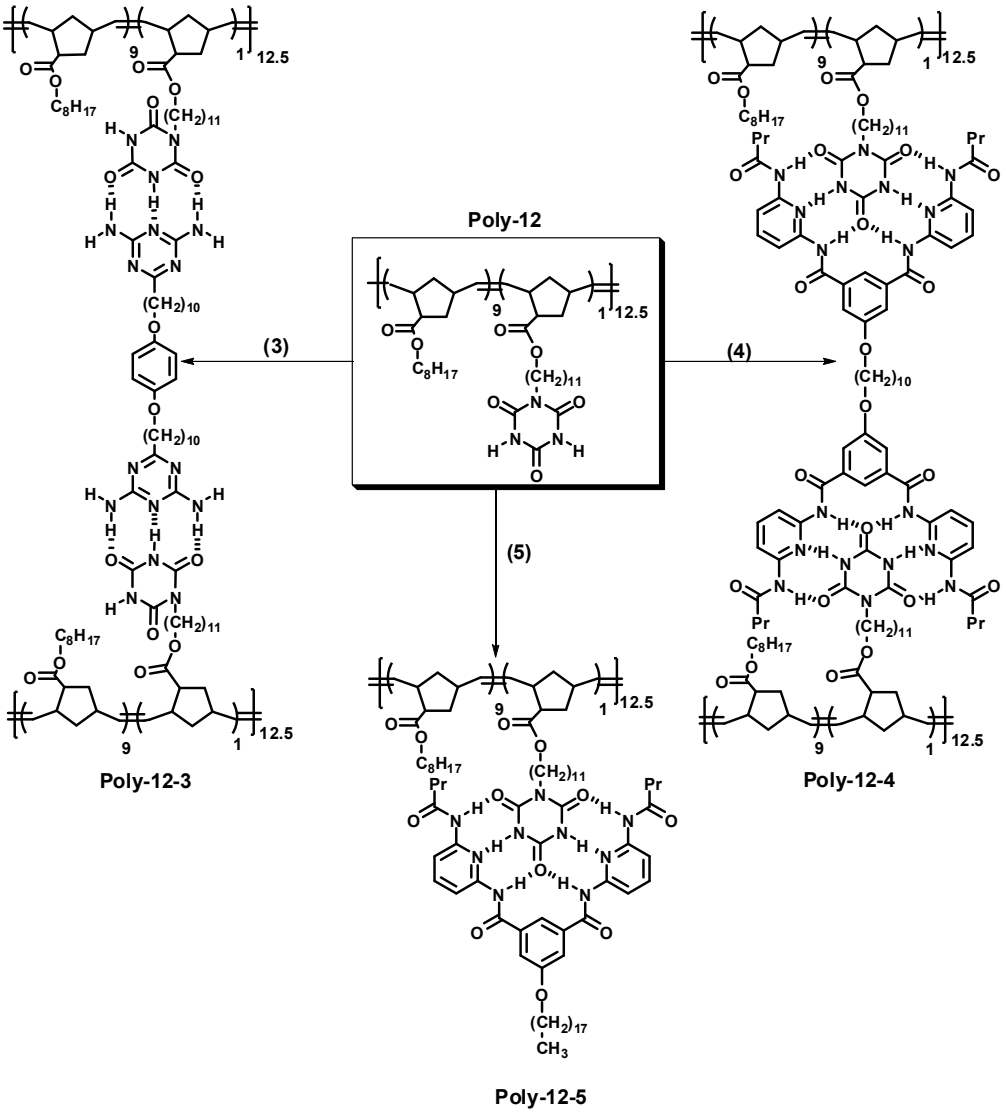
Copolymer composition and molecular weight are important parameters that affect the subsequent preparation of homogenous crosslinked polymer networks in 1-chloronaphthalene, which was the solvent of choice for all our rheological measurements because of its relatively high boiling point. The solubility 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 non-polar 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 non-polar solvents might be attributed to self-association of the cyanuric acid groups along the polymer backbone, which has been reported previously.[20] The copolymer composition

for our rheological measurements was chosen to be 10 mol% with respect to **2**, resulting in copolymers that were completely soluble in 1-chloronapthalene. The ability to prepare homogenous crosslinked samples in solution was also found to be affected by molecular weight. **Poly-12** was synthesized 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 weight%, which is attributed to self-association of pendant cyanuric acid groups. Lowering the degree of polymerization to 250 resulted in uniform polymer solutions with a polymer concentration of 5-10 weight%. However, the addition of crosslinking 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 weight% and formed homogenous, sTable polymer networks upon crosslinking.

5.6 Self-assembly and crosslinking studies

Before conducting crosslinking studies, the hydrogen bonding self-assembly between **2** and the monotopic compounds **5** and **6** were investigated 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 two equivalents of **6**, the imide signal of **2** shifted downfield from 9.57 ppm to 13.60 ppm while the amine proton signals of **6** shifted downfield from 5.58 ppm to 5.76 ppm. Further addition of another two

equivalents 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 ppm to 12.44 ppm upon the addition of one equivalent of **5**, while the amide proton signals of **5** shifted downfield from 8.93 ppm and 8.40 ppm to 9.85 ppm 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 ppm 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 **Poly-12** was crosslinked through hydrogen bonding self-assembly, using ditopic crosslinking agents **3** and **4** (Scheme 5.3).



Scheme 5.3 Noncovalent crosslinking and functionalization strategies for **Poly-12**: formation of (i) network **Poly-12-3** via the addition of crosslinking agent **3**, (ii) network **Poly-12-4** via the addition of crosslinking agent **4**, and (iii) functionalized **Poly-12-5** via the addition of the monotopic functionalization agent **5**.

The degree of crosslinking can be controlled easily via the amount of the crosslinking agent added. The crosslinking agent concentration was varied from 0% to 400% (molar ratio of functional groups in the crosslinking agent to cyanuric acid groups attached to the polymer chains). The crosslinked networks were characterized quantitatively using rheology but initial visual observations of the mechanical properties

provided a telling qualitative picture. Solutions of **Poly-12** yielded a low-viscosity fluid that readily flowed after vial inversion (center vial in Figure 5.3), while crosslinking **Poly-12** with **3** resulted in an elastic solid. The left vial in Figure 5.3 shows the vial-inversion experiment for a 100% crosslinking agent concentration where the gel did not flow even after several months. In contrast, when **Poly-12** was crosslinked with **4** at 100% crosslinking agent concentration, a highly viscous fluid was obtained. The right vial in Figure 5.3 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, indicative of a highly viscous liquid. The marked difference in flow behavior is indicative of different self-assembled micro-structures of the crosslinked materials. At first sight, it seems counterintuitive that the three-point crosslinking agent **3** results in an elastic gel, while the stronger six-point crosslinks with agent **4** result in a high-viscosity fluid. In order to quantitatively probe the effect of both crosslinking agents on network formation, rheological measurements with a cone-and-plate rheometer were carried out.

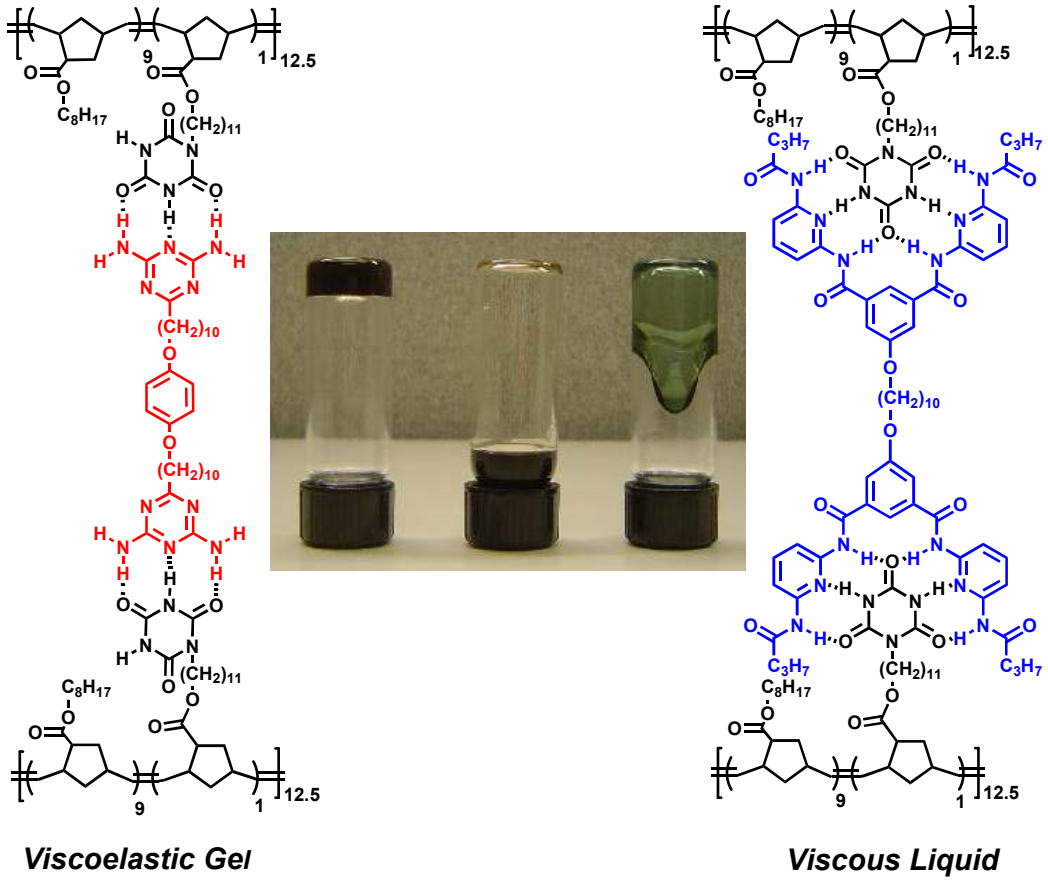


Figure 5.3 Optical micrograph of inverted vials 3-4 hours after vial inversion with (left) the stable elastic gel **Poly-12-3**, (center) the pure uncrosslinked **Poly-12** and (right) the crosslinked viscous liquid **Poly-12-4**. All polymers and additives were dissolved in 1-chloronaphthalene.

5.7 Rheological characterization

Initially the presence of self-association of the cyanuric acid group in the uncrosslinked **Poly-12** was investigated. This study was important to determine if there is any appreciable rheological effect due to self-association of the cyanuric acid functional groups. As a control experiment, the rheology of the pure polymer solution **Poly-12** with **Poly-12-5** was compared. 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. In the presence as well as

absence of **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 of 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 crosslinking by using complementary hydrogen bonding interactions.

Furthermore, the mechanical properties of the crosslinked networks were investigated. The strain amplitude sweeps of **Poly-12-3** and **Poly-12-4** are shown in Figure 5.4. The amplitude sweep is an oscillatory test with variable amplitude and constant frequency values, in which the elastic and loss moduli are measured. The elastic or storage modulus is a measure of the deformation energy that is stored in the sample during the shear process and recovered after the load is removed by shearing in the opposite direction or releasing the stress. On the other hand, the loss modulus is a measure of the energy that is dissipated in the sample during the shear process and rendererd mechanically useless as thermal energy. For both experiments the polymer concentration was 10 weight% and the crosslinking 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 5.3. 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

crosslinking agent **4** increases the viscosity of the network but does not result in the formation of a viscoelastic gel.

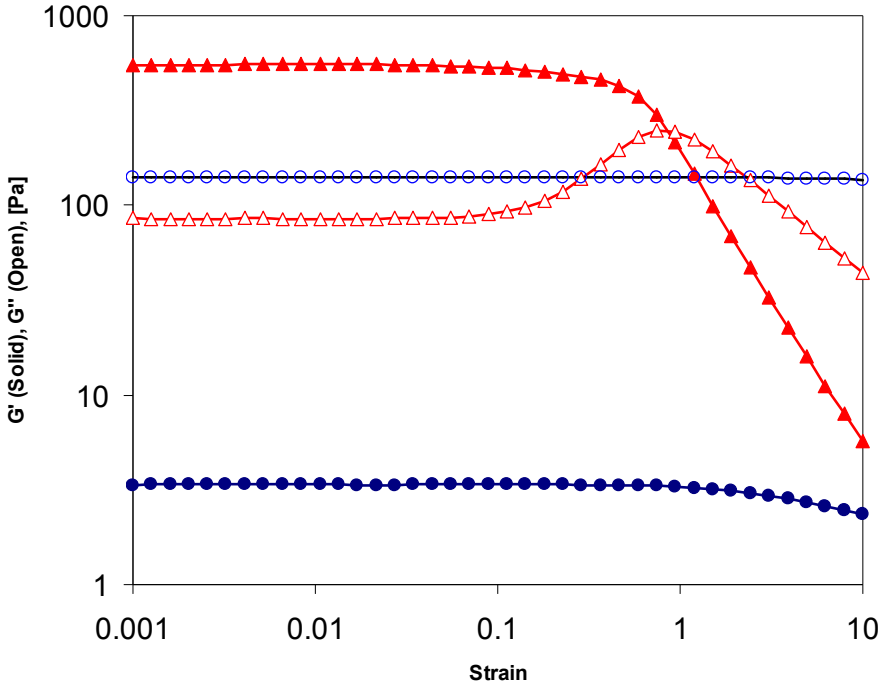
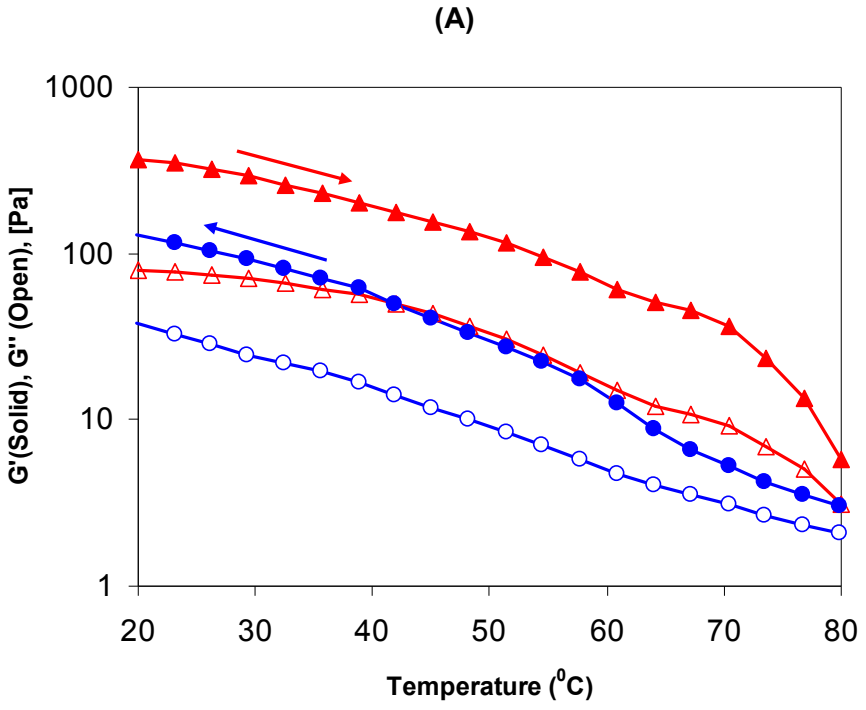


Figure 5.4 Strain amplitude sweep at 20°C at ω = 6.3 rad/s for **Poly-12-3** (triangles) and **Poly-12-4** (circles).

In order to probe the thermal reversibility of the polymer networks, a temperature sweep was carried out 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 as well as the cooling cycle the viscoelastic moduli were monitored at a constant frequency (1 Hz = 6.28 rad/s) and strain amplitude (0.1). At high temperatures, this protocol can lead to low signal to noise ratio, 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 5.5 show a strong temperature dependence of the network. Both

samples showed gradual but large decreases of the dynamic moduli over the temperature range without sharp transitions. The decrease in moduli of both crosslinked 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 Pa.s to 0.0013 Pa.s over the same temperature range, and can thus be attributed to the break-up of hydrogen bonded intermolecular associations. The crosslinking 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 5.5 (A). The recovery of these gels after cooling is also markedly different. Both samples show reversible increases of the moduli during the cooling cycle. **Poly-12-3** exhibits significant hysteresis, while the viscous **Poly-12-4** recovers almost quantitatively.



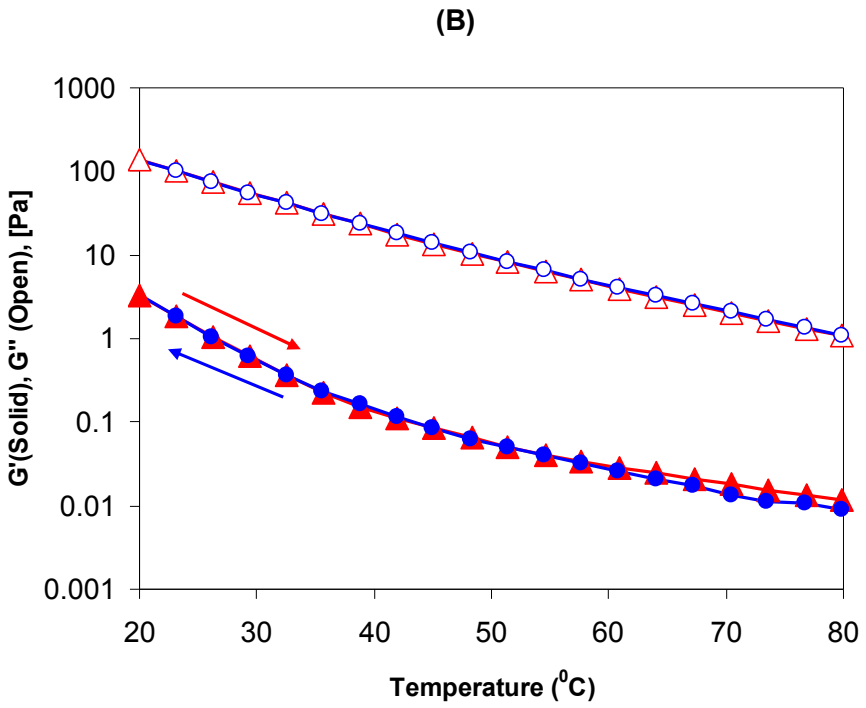


Figure 5.5 Temperature sweep profile: (A) **Poly-12-3** and (B) **Poly-12-4**. The red curves (triangles) denote the heating curves from 20 to 80 °C. The blue curves (circles) denote the cooling curves from 80 to 20 °C. G' and G'' were measured at $\omega = 6.3$ rad/s and strain amplitude 0.1.

To probe the thermal recovery and rheological behavior at high temperatures in more detail, three frequency sweeps were carried out 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 minutes. The results are presented in Figure 5.6 for both crosslinking 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 $G' > G''$ at all accessible frequencies, 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 5.5. Careful analysis of the rheological data in Figures 5.5 and 5.6 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 minute resting period. It is hypothesized that the lack of polymer mobility in the crosslinked gel (**Poly-12-3**) hinders the recovery of mechanical properties after cooling in comparison to the viscous liquid **Poly-12-4**. Although Figure 5.6 does not show a complete study of the temperature-dependent frequency sweeps, which 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 simultaneously 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.

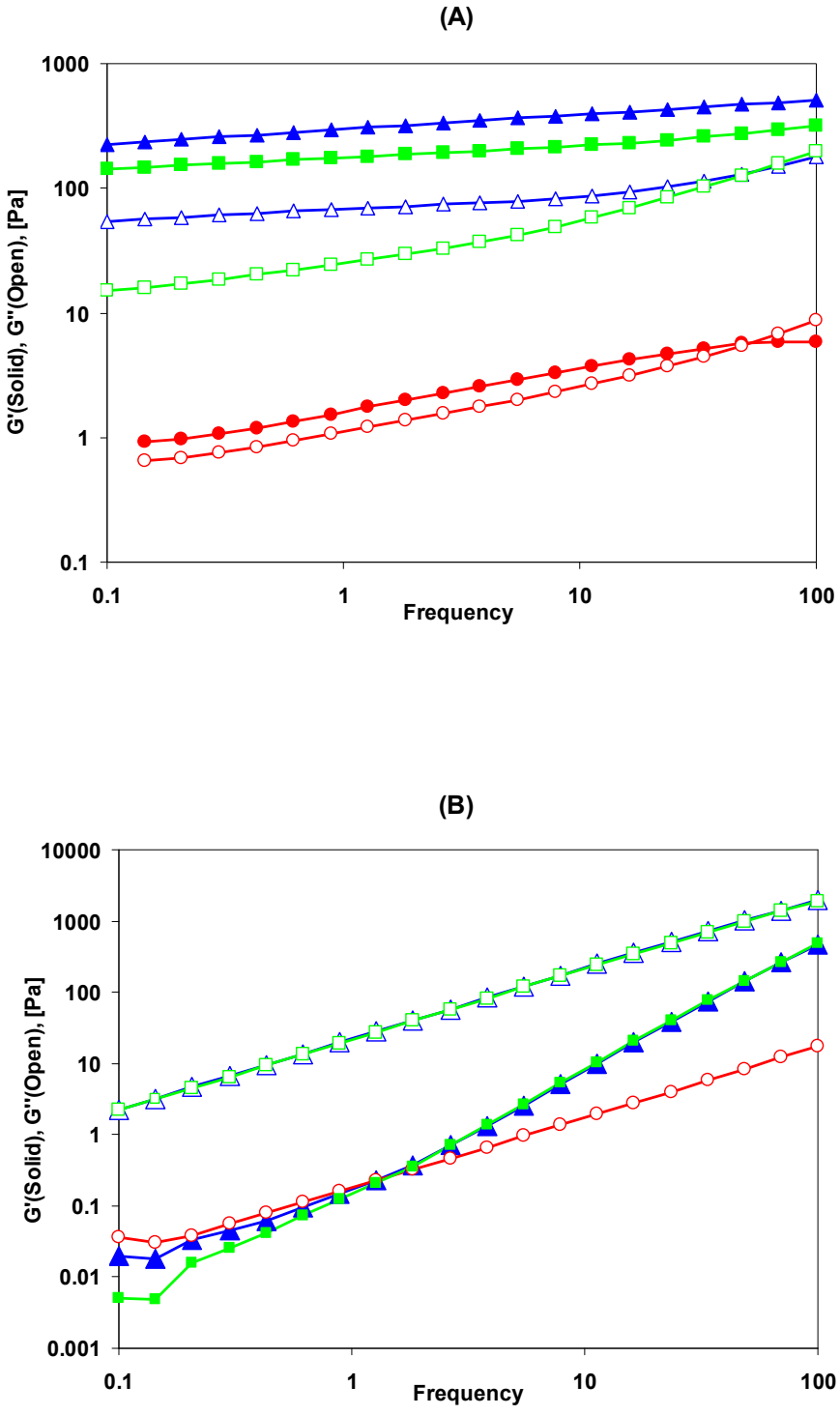


Figure 5.6 Frequency sweep profile: (A) **Poly-12-3** and (B) **Poly-12-4**. First sweep at 20 °C (triangles), second sweep at 80°C (circles) and third sweep at 20°C (rectangles), at

strain amplitude 0.1. G' data for **Poly-12-4** at 80°C has been omitted because of insufficient rheometer sensitivity.

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

Figure 5.7 displays the crosslinking profile of **Poly-12-3**, in which the elastic and the loss moduli of **Poly-12-3** are plotted as a function of crosslinking 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 cross-over or gelation concentration, since the elastic modulus becomes greater than the loss modulus and elastic gel-like properties are observed.

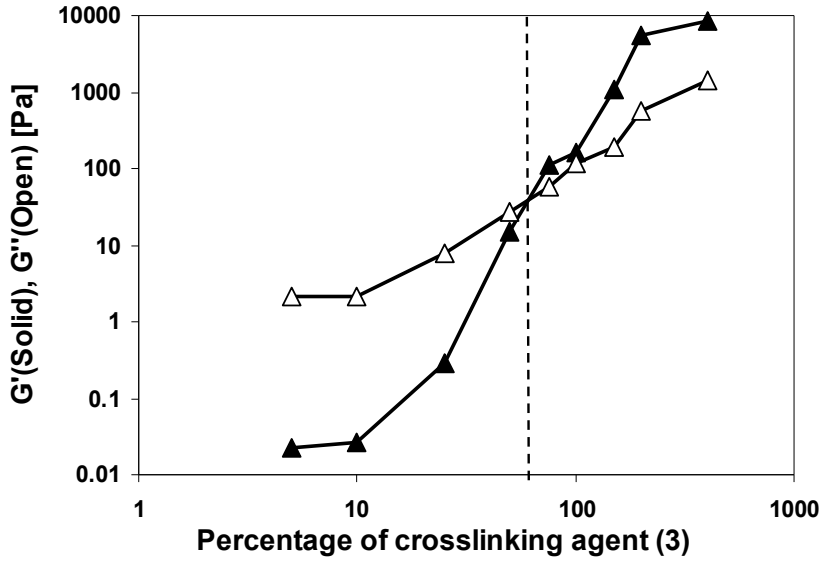


Figure 5.7 Crosslinking profile of **Poly-12** using **3**. Filled symbols denote the elastic modulus [*G′*], whereas empty symbols denote the loss modulus [*G″*] at strain value of 0.1. The percentage of **3** is based on the molar ratio to cyanuric acid groups attached to the polymer.

Figure 5.8 displays the crosslinking profile of **Poly-12-4**. In contrast to Figure 5.7, 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 crosslinking agent, since the loss modulus reaches even higher values for than the elastic modulus found at analogous concentrations of **3**.

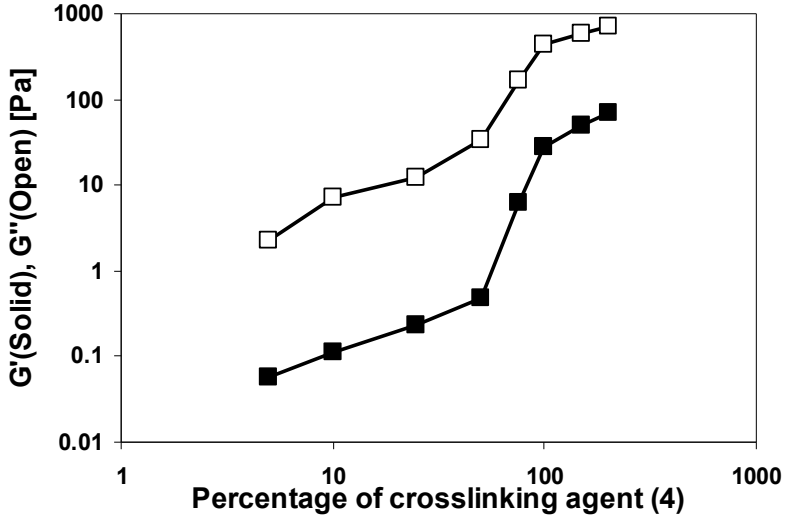
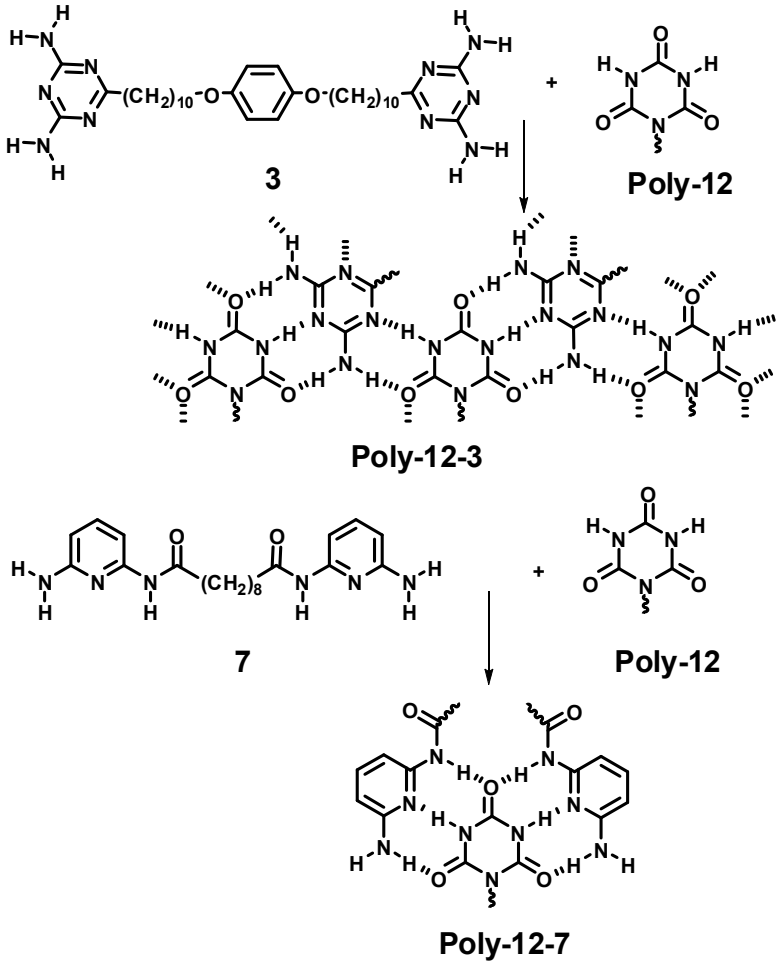


Figure 5.8 Crosslinking profile of **Poly-12** using **4**. Filled symbols denote the elastic modulus [*G′*], whereas empty symbols denote the loss modulus [*G″*] at strain value of 0.1. The percentage of **4** is based on the cyanuric acid groups attached to the polymer.



Scheme 5.4 Proposed network micro-structures for **Poly-12-3** and **Poly-12-7**.

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 crosslinking of several polymer chains without the high level of connectivity that characterizes a gel. Because of higher interaction strengths of the individual interaction between the six point hydrogen bonded complex between Hamilton wedge and cyanuric acid (K_a ~10^6 M^{-1} in chloroform at room temperature)[1] 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 timescales between

crosslinking agent and polymer backbone, which could change the relaxation timescales of the network. Instead, the data suggest a difference in the micro-structure of the networks. At first sight, there is no obvious reason, because both crosslinking agents are ditopic. A closer inspection of the molecular structure of **Poly-12-3** in Scheme 5.3, 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 crosslinking agent molecules (illustrated in Scheme 5.4). As a result, each 2,4-diaminotriazine-based crosslinking agent **3** would potentially be connected to up to 4 cyanuric acid residues via two and three point hydrogen bonding, while the Hamilton-wedge based crosslinking agent **4** is limited to interactions with maximum 2 cyanuric acid residues. The resulting higher connectivity of **Poly-12-3** would explain the formation of 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 crosslinking 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 crosslinking agent **7** should result in a true three-point hydrogen bonding interaction with the cyanuric acid groups and multi-point array formation should not be possible. Indeed, it was found that the addition of crosslinking agent **7** to **Poly-12** resulted in free-flowing viscous liquids, even at the highest crosslinking 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 multi-point 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 crosslinking agent loading are illustrated in Figure 5.10, 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.

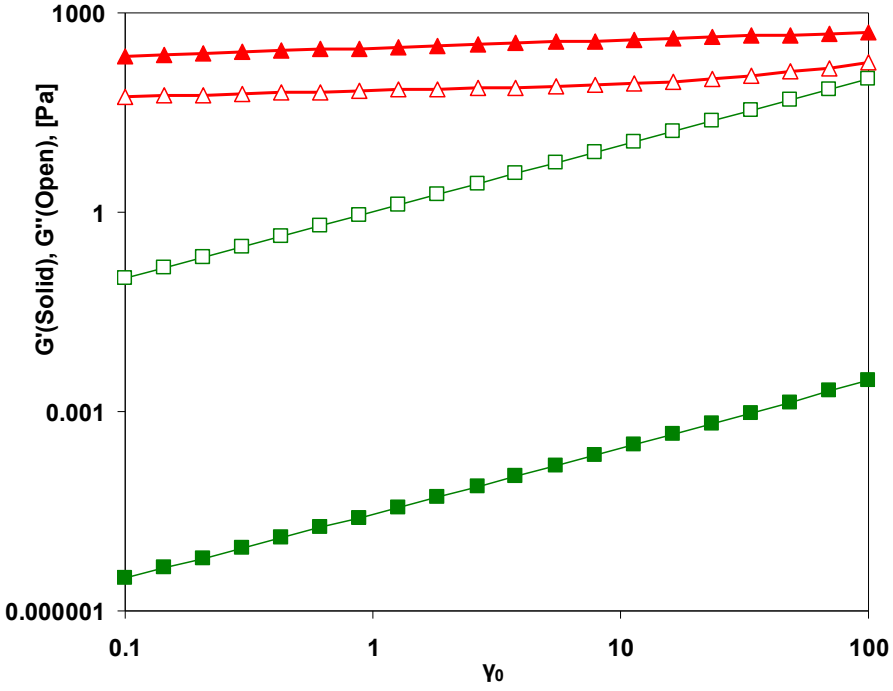


Figure 5.10 Frequency sweep profile at 20°C: (A) **Poly-12-3** (triangles), and (B) **Poly-12-7** (rectangles), at strain amplitude 0.1.

5. 8 Summary and future outlook

In this chapter, random copolymers containing cyanuric acid recognition units via ROMP have been synthesized and their crosslinking behavior via complementary hydrogen bonding has been investigated. The hydrogen bonding recognition system consisted of the interaction between cyanuric acid units along the polymer backbone and

small molecule ditopic crosslinking agents based on either 2,4-diaminotriazine or Hamilton wedge motifs. This crosslinking system, by combining a functional group tolerant polymerization route with noncovalent crosslinking techniques, allows for the facile synthesis of reversible crosslinked polymers with a high degree of control over the extent of crosslinking 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 crosslinking agent. Our approach results in the creation of materials with diverse mechanical properties from the same parent polymer backbone.

5.9 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**,[13] spacer monomer **1**,[6] N-(6-aminopyridin-2-yl) butyramide,[8] 5,5'-(decane-1,10-diylbis(oxy))diisophthalic acid,[21] 1,4-bis (10-bromodecyloxy) benzene,[22] and 6-dodecyl-1,3,5-triazine-2,4-diamine (monotopic diaminotriazine),[23] N^1,N^{10}-bis(6-aminopyridin-2-yl)decanediamide **7**[24] were synthesized according to published procedures. 1-chloronaphthalene, dicyandiamide, and 5-octyldecyloxy isophthalic acid were used as received.

Characterization procedure

As reported in Chapter three.

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 hrs. 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 x 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, -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 (0.75g, 0.0124 mol) and KOH (1.00 g) were dissolved in 1-propanol (100 mL) and the reaction mixture was refluxed for 12 hours. 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 (t, 4H, -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(N1,N3-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 hours 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 twelve hours 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 dried. The residue was suspended in ethyl acetate and stirred for 30 minutes 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.

N1, N3-Bis(6-butyramidopyridin-2-yl)-5-(octadecyloxy)isophthalamide (6)

5-Octyldecyloxy isophthalic acid (2.5 g, 0.005 mol) was dissolved in thionyl chloride (5mL) and a few drops of DMF were added. The reaction mixture was heated at 80 °C for 4 hours 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 (3.00g, 0.016 mol) and NEt_3 (20 mL) in anhydrous THF (100 mL) at 0°C. The solution was stirred at room temperature for twelve hours, 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 (2.321g, 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 and the reaction was monitored by observing the olefinic signals of the monomer by ^1H 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 hours to remove all the solvent. The ^1H and ^{13}C NMR spectra of all copolymers are analogous to the ones reported in the literature.[6]

Crosslinking experiments

For all crosslinking experiments, the copolymers were dissolved in a calculated amount of 1-chloronaphthalene and the mixture was stirred overnight at room temperature to ensure a homogenous solution. Then, a calculated amount of the crosslinking agent was added and the mixture was stirred briefly at elevated temperature until a homogenous solution was obtained. The sample was then allowed to rest at room temperature for twelve hours before the rheological experiments were carried out.

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 weight%). Then 22.76 mg (0.074 mmol based on the hydrogen bonding sites allowing for quantitative crosslinking) of **3** was added to the sample and the suspension was heated until a clear homogenous solution was obtained, which quickly gelled when cooled to room temperature. The gel was then allowed to rest at room temperature for least twelve hours before rheological measurements were carried out.

Rheological characterization

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 50mm, angle 1°).[25] All measurements were carried out in oscillatory mode in order to probe the equilibrium structures of the polymer solutions.

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), 6) temperature sweep (80 to 20°C; γ = 0.01; ω = 6.28 rad/s) to investigate thermal reversibility, and 7) frequency sweep at constant strain amplitude (20°C; γ = 0.1; ω = 0.1-100 rad/s) to determine the extent of thermal recovery.

5.10 References

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CHAPTER SIX

Complementary Hydrogen Bonded Crosslinked Polymer Networks Based on Thymine Moieties

6.1 Abstract

Complementary hydrogen bonded crosslinked polymer networks based on thymine residues attached to the polymer backbone have been synthesized by using a combination of ROMP and hydrogen bonding interactions. The thymine residue represents a single ADA motif and hence the recognition units used for crosslinking were based only on three point hydrogen bonding interactions. The crosslinked polymer networks synthesized were thermally reversible and the network properties were dependent upon the molecular structure of the crosslinking agent used. The addition of the 2,4-diaminotriazine as well as the Hamilton wedge crosslinking agents produced freely flowing to highly viscous liquids respectively and it was seen that the addition of the ditopic Hamilton wedge crosslinking agent resulted in the highest increases in the solution viscosity. However, none of the compositions exhibited a true viscoelastic solid formation, which can be attributed to the lack of network formation capability in the thymine system with only one ADA face in comparison to the cyanuric acid system with two ADA faces which were able to form viscoelastic solids with the 2,4-diaminotriazine crosslinking agents via multi-point hydrogen bonding interactions. Hence, it was seen that by varying the type of hydrogen bonding motif used for crosslinking, materials with different rheological properties could be obtained, indicating that the network microstructure plays an important role in physical properties of these networks.

6.2 Introduction

In Chapters one and two the importance of hydrogen bonding interactions in reversible crosslinking of polymers was described. Furthermore, Chapter five outlined the importance of using complementary hydrogen bonding interactions, to control the network structure and the final mechanical properties of the crosslinked network, i.e. by changing the complementary hydrogen bonding recognition units used for inter-chain crosslinking, the cyanuric acid copolymer was converted into either a highly viscoelastic gel or highly viscous liquid. In this chapter the effect of a subtle change in molecular architecture of the hydrogen bonding recognition moiety is investigated, as the cyanuric acid functional group is replaced by a thymine functional group. The effect of molecular architecture of the crosslinking agent as well as the hydrogen bonding motifs used for inter-chain crosslinking on the properties of these networks is discussed. It will be demonstrated that subtle changes in the molecular architecture of the interacting moieties results in dramatic changes in the physical properties of these materials. Such a study will provide useful insights for 'Structure-property" relationship in reversibly crosslinked materials design based on complementary hydrogen bonding interactions.

6.3 Research design

The research design consists of random copolymers functionalized with thymine residues as hydrogen bonding sites. In contrast to the cyanuric acid residues, the thymine groups have a single ADA face and as a result can only form three point hydrogen bonding interactions with both 2,4-diaminotriazine and 2,6-diaminopyridine groups. The noncovalent functionalization of 2,4-diaminotriazine as well as 2,6-diaminopyridine side-chain functionalized polymers using substituted thymines has been

studied before.[1-4] It has also been reported that the association constants of the two complexes of 2,4-diaminotriazine and 2,6-diaminopyidine with thymine are very similar.[5] The hydrogen bonding self-assembly motifs used for inter-chain crosslinking are shown in Figure 6.1.

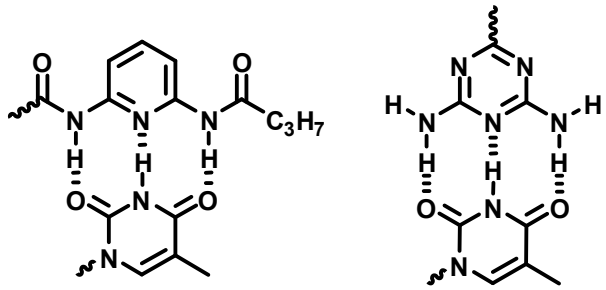


Figure 6.1 Self-assembly motifs employed in this study: (A) three point hydrogen bonded complex between 2,6-diaminopyridine and thymine and (B) three point hydrogen bonded complex between 2,4-diaminotriazine and thymine.

The monomers and the crosslinking agent used in this study are depicted in Figure 6.2. In this study the thymine functional groups are anchored covalently onto a poly(norbornene) backbone by copolymerizing **1** with **2** using ROMP, to form **Poly-12**. As explained in Chapter five, monomer **1** serves as a diluent and increases solubility of the polymer in non-polar solvents. Hydrogen bonded crosslinking was carried out by employing either 2,4-diaminotriazine based crosslinking agents **5** and **7** or Hamilton wedge receptors based crosslinking agents **4** and **6**. As described in Chapter 5, all crosslinking processes as well as all characterizations of the resulting crosslinked polymer networks were carried out in 1-chloronaphthalene, a non-competitive, high boiling solvent in which all copolymers have good solubility.

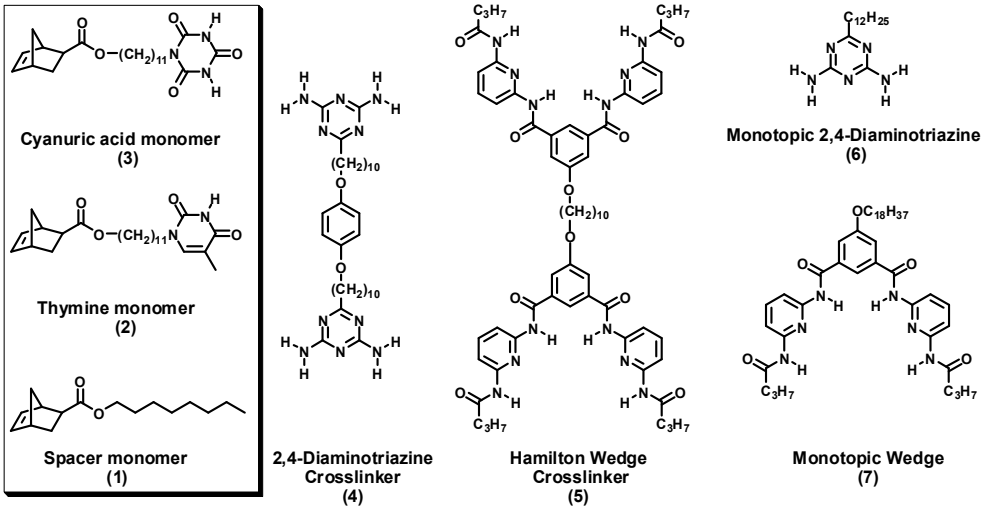


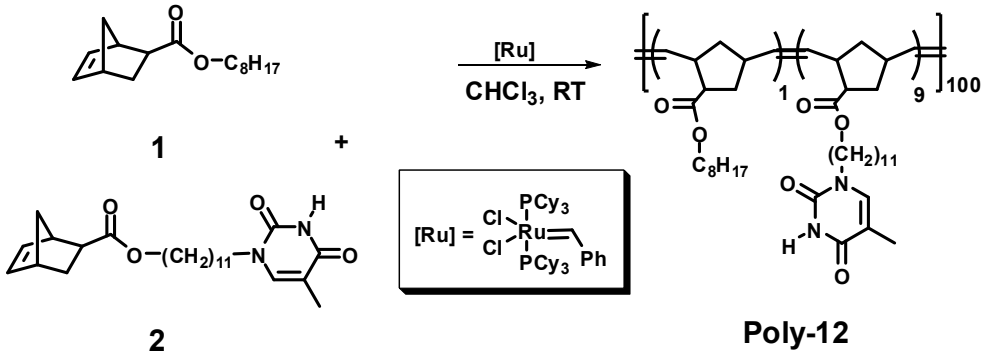
Figure 6.2 Monomers **1-3**, functionalized monotopic and ditopic agents **4-7** utilized in this study.

6.4 Results and discussions

6.4.1 *Polymerization studies*

The detailed polymerization behaviors of monomers **1** and **2** have been previously reported, which can be copolymerized in a statistical manner via ROMP in chloroform at room temperature using Grubbs' first generation initiator (Scheme 6.2).[6,2] The ROMP copolymerization of these monomers resulted in polymers with controlled molecular weighs and relatively low polydispersities. Table 6.1 lists the gel-permeation chromatography characterization of these polymers. The polymer compositions and molecular weights were found to be important parameters affecting the subsequent syntheses of homogenous crosslinked polymer networks in 1-chloronaphthalene. The polymers were designed to possess low concentrations of the thymine monomer, in order to study crosslinking while simultaneously maintaining good solubility in 1-chloronaphthalene**.** In Chapter 5 it was seen that the solubility of the cyanuric acid functionalized polymer (**Poly-13**) in 1-chloronaphthalene was highly dependent upon the

mole fraction of **3** and the degree of polymerization, this phenomenon was explained due to the self-association of the cyanuric acid groups. In contrast to **Poly-13**, it was found that **Poly-12** exhibited very good solubility in 1-chloronaphthalene even at 30 mol% of **2** and at a degree of polymerization as high as 1000.



Scheme 6.1 Synthesis of **Poly-12** by random polymerization of monomers **1** and **2**.

Table 6.1 GPC data of unfunctionalized copolymers **Poly-12**. Polymer abbreviations are based on Scheme 6.2.

Entry	mol% of 2	[M]/[I]	M_n (10^3)	M_w (10^3)	PDI
Poly-12	10	125	46	71	1.56
Poly-12	10	1000	244	322	1.32

6.4.2 *Self-assembly studies*

To investigate the effect of the self-association of cyanuric acid and the thymine residues on the polymer solubility, the self-association characteristics of monomers **2** and

3 were probed. Hence, ^{1}H NMR spectroscopy dilution experiments in deuterated chloroform at room temperature were conducted and it was found that both the monomers displayed self-association and that the self-association was slightly higher in the case of **3** as compared to **2**.[1,7] This can be explained on the basis of the presence of two ADA faces per cyanuric acid group increasing the propensity for self-association as compared to only single ADA face per thymine residue which could explain the tendency of **Poly-13** to phase separate at higher molecular weights and higher concentrations in 1-chloronaphthalene as compared to analogous polymers based on **Poly-12**.

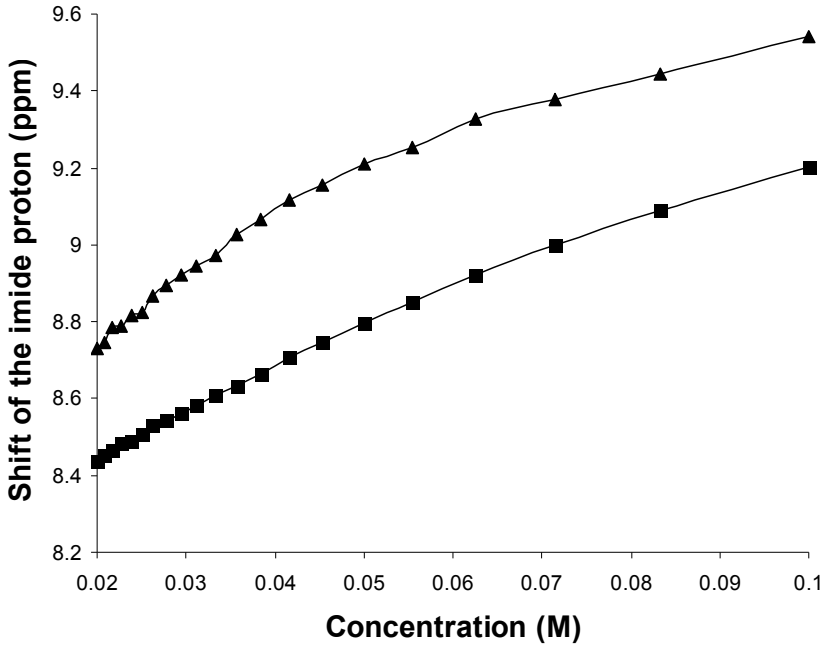


Figure 6.3 Chemical shift in ppm of the imide proton (N-H) of **2** (squares) and **3** (triangles) as a function of concentration in chloroform at room temperature.

Before conducting the crosslinking studies, the hydrogen bonding self-assembly between model compounds which consisted of the monomer **2** and the monotopic compounds **6** and **7** was studied using ^{1}H NMR spectroscopy at room temperature. The self-assembly was probed by monitoring the shifting of the amine proton signal of **6**,

amide proton signals of **7** and the imide proton signal of monomer **2** before and after self-assembly. The self-assembly was performed using a 0.2 M solution of the compounds in deuterated chloroform. The imide signal of **2** shifted downfield from 9.47 ppm to 12.98 ppm upon the addition of one equivalent of monotopic **6,** while the amine proton signals of **6** shifted downfield from 5.83 ppm to 7.44 ppm. Further addition of another three equivalents of **6** resulted in the downfield shift of the imide proton to 13.60 ppm, whereas the amine proton signal of **6** was shifted to 5.97 ppm. The imide signal of monomer **2** shifted downfield from 9.47 ppm to 11.81 ppm upon the addition of half equivalent of monotopic wedge **7,** while the amide proton signals of **7** shifted downfield from 8.76 ppm and 8.53 ppm to 9.93 ppm and 9.57 ppm respectively. Further addition of another half equivalent of **7** resulted in the downfield shift of the imide proton of **2** to 12.23 ppm, whereas the amide proton signal of **7** was shifted to 9.56 ppm and 8.89 ppm. These results demonstrate the strong hydrogen bonding interactions between monomer **2** and **Poly-12** with **6** and **7**.

6.4.3 *Crosslinking studies*

After studying the self-assembly of **Poly-12**, the polymer scaffold was reversibly crosslinked via complementary hydrogen bonding interactions using crosslinking agents **4-7**. Crosslinking agents **4** (two 2,4-diaminotriazine functional groups) and **7** (two 2,6-diaminopyridine functional groups) acted as ditopic crosslinking agents whereas crosslinking agent **5** acted as a tetra-topic crosslinking agent, as **5** has four 2,6-diaminopyridine functional groups. MonoDAT (**6**) acted only as a functionalization agent and did not cause any inter-chain crosslinking but resulted only in end-capping the

polymer. The detailed network and functionalized structures of **Poly-12** are depicted in Figure 6.4.

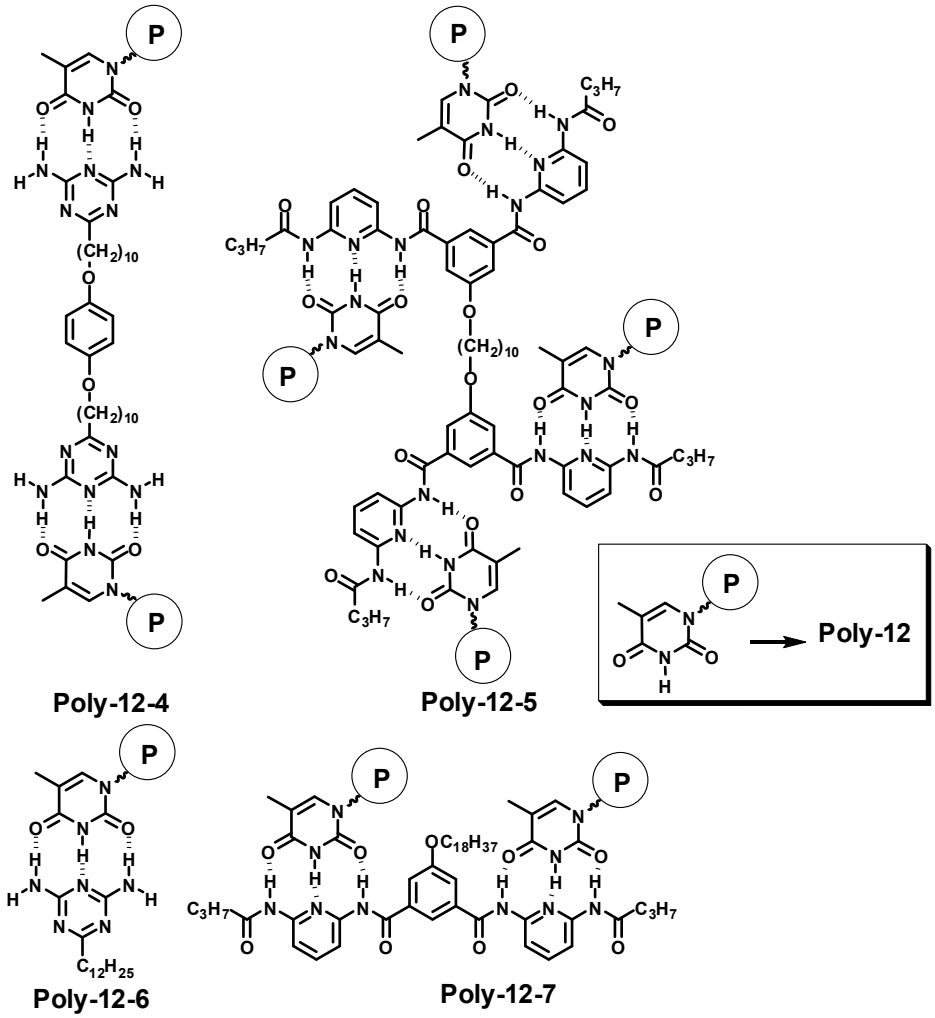


Figure 6.4 Microstructures of networks based on **Poly-12**: crosslinked networks – **Poly-12-4**, **Poly-12-5**, **Poly-12-7** and functionalized **Poly-12-6**.

Crosslinking studies using **Poly-12** having a degree of polymerization equal to 125 at 10% (wt) solution were first conducted. However it was found that for **Poly-12** the network samples obtained after crosslinking were free-flowing liquids and resulted in insufficient rheometer sensitivity. Hence, in order to obtain data of reasonable magnitude

Poly-12 with a DP of 1000 was synthesized. By increasing the molecular weight it was able to get an increase in the signal strength by a factor of almost 1000 and thus obtain data with a high degree of accuracy.

6.5 Crosslinking behaviors of Poly-12 and Poly-13

Although **Poly-12** and **Poly-13** have very similar structures, they displayed significantly different behaviors on crosslinking with compounds **4**-**7**. For example, ditopic **4** was an efficient crosslinking agent for **Poly-13** which produced highly viscoelastic solids at ca. 0.6 and higher equivalents of **4.** However, in the case of **Poly-12** even after adding one equivalent of **4**, no viscoelastic solid was formed, instead significant increase in the solution viscosity was observed. This difference in the physical properties of these two seemingly similar polymer networks can be attributed to the differences in the network micro-structures based on Scheme 5.4 (Chapter 5) and Figure 6.4 (Chapter 6). **Poly-13-4** represents a true three dimensional polymer network with a strong continuity where each crosslinking agent molecule binds several polymer chains through multiple hydrogen bonding interactions, whereas the **Poly-12-4** represents a weakly connected network where each crosslinking agent molecule binds only two polymer chains.

Table 6.2 $G'/\ G''$ and $|G^*|$ values for unfunctionalized, crosslinked and functionalized polymers of **Poly-12** and **Poly-13**.

Crosslinking Agent		Poly-13 (DP=125)		Poly-12 (DP=1000)	
		G'/G''	$\|G^*\|$	G'/G''	$\|G^*\|$
None	**Eq**	<0.0001	3.32	<0.0001	14.57
4	**1.0**	0.95	526.73	0.04	35.04
5	**1.0**	0.28	0.29 (10^4)	0.06	66.63
6	**1.0**	4.62	12.94 (10^4)	<0.0001	10.40
7	**1.0**	<0.0001	2.72	0.04	23.62

After studying the crosslinking profile of the **Poly-12** and **Poly-13** using ditopic agent **4**, the effect of monotopic **6** on these polymers was investigated. Even though **6** was monotopic, it effectively crosslinked **Poly-13** through multiple hydrogen bonding interactions leading to highly viscoelastic solids. The addition of one equivalent of **6** to **Poly-13** transformed it from a free flowing liquid to a viscoelastic solid. In stark contrast, the addition of **6** to **Poly-12** resulted in lowering of the solution viscosity, with the addition of one equivalent of **6** to **Poly-12** resulting in a lowering of both G' and G'' by nearly 0.3 times as compared to pure polymer. This phenomenon can be explained by the fact that thymine and 2,4-diaminotriazine form a 1:1 complex as a result, **6** acts as an endcapping agent for the thymine residues of **Poly-12**. Hence the addition of **6** to **Poly-12**

caused functionalization of the thymine residues which then severely suppressed the self-association of the thymine residues, thereby decreasing the G' and G'' values.

The six point wedge Hamilton-cyanuric acid complex has a K_a value of around 10^6 M^{-1},[8,9] hence it was not very surprising that **5** efficiently crosslinked **Poly-13**, resulting in highly viscous liquids **Poly-13-6**. The addition of one equivalent of **6** to **Poly-13** transformed the sample from a free flowing liquid to a highly viscous network. Crosslinking agent **5** has four 2,6-diaminopyridine functional groups hence it can effectively bind four thymine residues per molecule of crosslinking agent and can act as a tetrafunctional crosslinking agent for **Poly-12**. Therefore, as expected the addition of **5** to **Poly-12** resulted in an increase in the solution viscosity to form highly viscous liquids, upon the addition of one equivalent of **5** to **Poly-12**.

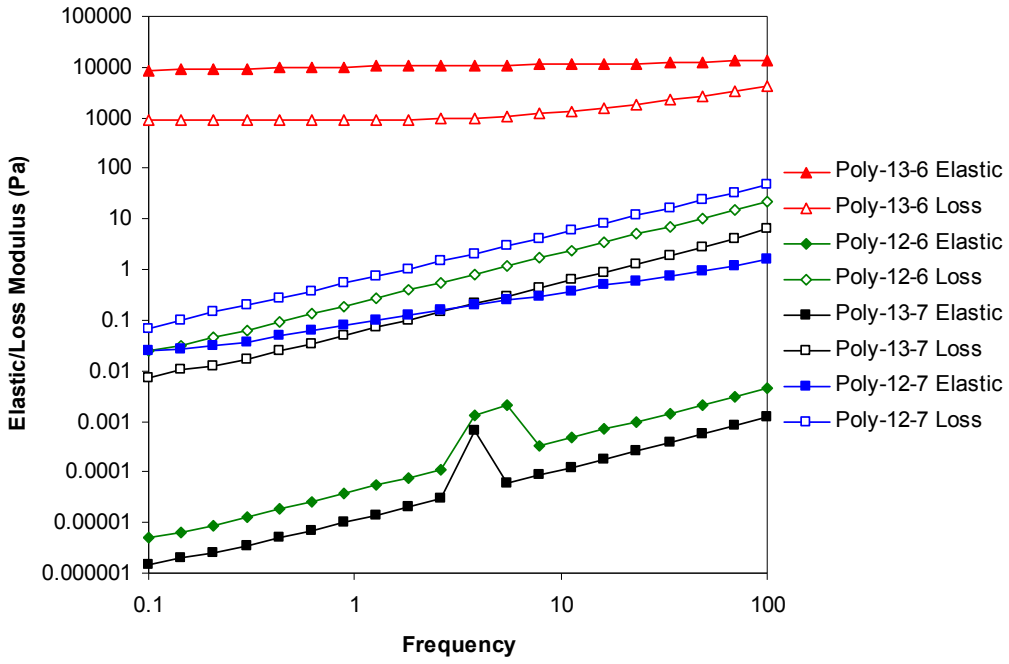


Figure 6.5 Frequency sweep Profile at strain amplitude 0.1 and 20°C: **Poly-13-6** (triangles), **Poly-12-6** (diamonds), **Poly-13-7** (squares) and **Poly-12-7** (rectangles).

The addition of monotopic wedge **7** to **Poly-13** did not cause any crosslinking as **7** was designed to be an end-capping agent for **Poly-13**, and the addition of **7** resulted only in functionalization of the cyanuric acid groups as shown in Figure 6.4. However, monotopic wedge receptor **7** has two 2,6-diaminopyridine groups as a result it can complex two thymine residues leading to a marginal increase in the moduli.

Since the addition of agents **4-7** to **Poly-12** resulted in mainly viscous liquids, flow experiments to probe the nature of these liquids were conducted. It was found that the complex solution viscosity of these networks had little dependence on the shear rate (Figure 6.6).

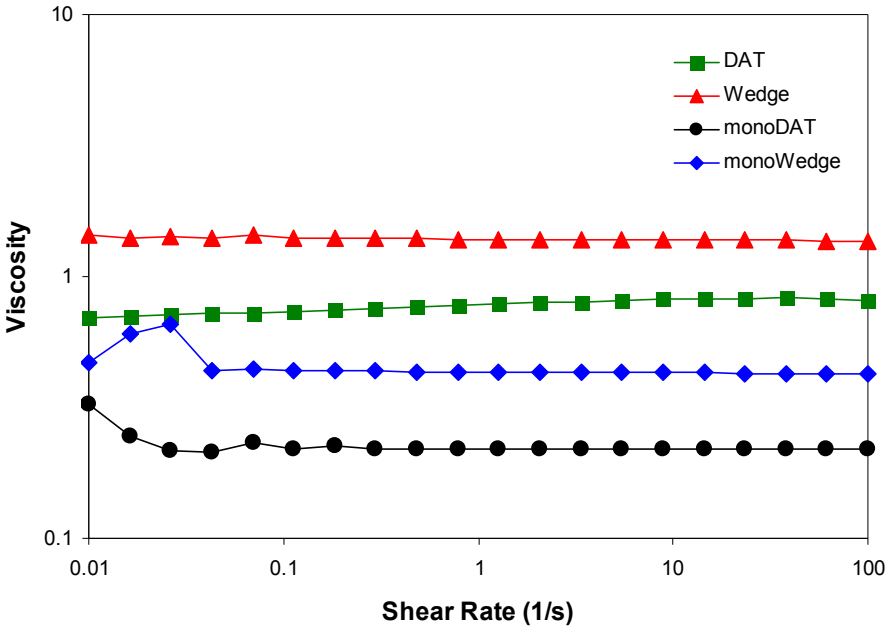


Figure 6.6 Flow curves for samples based on **Poly-12** at 20°C: **Poly-12-5** (triangles), **Poly-12-4** (squares), **Poly-12-7** (diamonds) and **Poly-12-6** (circles).

6.6 Effect of addition of more than one equivalent of crosslinking agent on the network properties of Poly-12

In complementary hydrogen bonded polymer networks, the degree of crosslinking can be varied easily by controlling the amount of the crosslinking agent added to the polymer. Hence, it is expected at exactly one equivalent of the crosslinking agent added, the system would represent a completely crosslinked system and further addition of the crosslinking agent should not cause any further crosslinking. However, the addition of more than one equivalent of the crosslinking agent can lead to functionalization of the polymer and thus cause "decrosslinking" of the network. For **Poly-13** the addition of more than one equivalent of **4**, **5** and **6** did not result in decrosslinking. However at higher equivalents, the increase in the G' and G'' leveled off. Such a phenomenon may be explained by the fact that cyanuric acid moieties having two ADA faces can result in multiple hydrogen bonding interactions which lead to a stable three-dimensional network and increasing the concentration of the crosslinking agent above one equivalent does not displace the network structure sufficiently to cause decrosslinking by functionalization of the polymer chains. However in the case of **Poly-12** which has only one ADA face, the effect of saturation is seen due to the functionalization of the polymer chains. Hence, when more than one equivalent of crosslinking agents **4**, **5** and **7** are added, a decrease in the G' and G'' was observed. However the exact concentration at which the effect of decrosslinking was observed was different for each agent. For instance the addition of 1.5 equivalents of **4** resulted in decrease in the G' and G'' whereas the effect of decrosslinking was observed only at two equivalents of **5** and **7**. The results of the decrosslinking of **Poly-12** is shown in Figure 6.7, where the G'' is plotted as a function of the concentration of the crosslinking agent.

Ditopic wedge **5** and monotopic wedge **7** differ only in the number of 2,6-diaminopyridine groups per molecule, where **5** has four groups and **7** has only two groups. As a result **5** acts as a tetrafunctional crosslinking agent while **7** acts as a difunctional crosslinking agent for **Poly-12**. It was observed that **5** was a superior crosslinking agent as compared to **7**. This can be attributed to the increased network density due to the higher functionality of **5**. The functionality of the crosslinking agent is an important parameter affecting the network strength, where the higher functionality of the crosslinking agent results in more efficient network crosslinking.

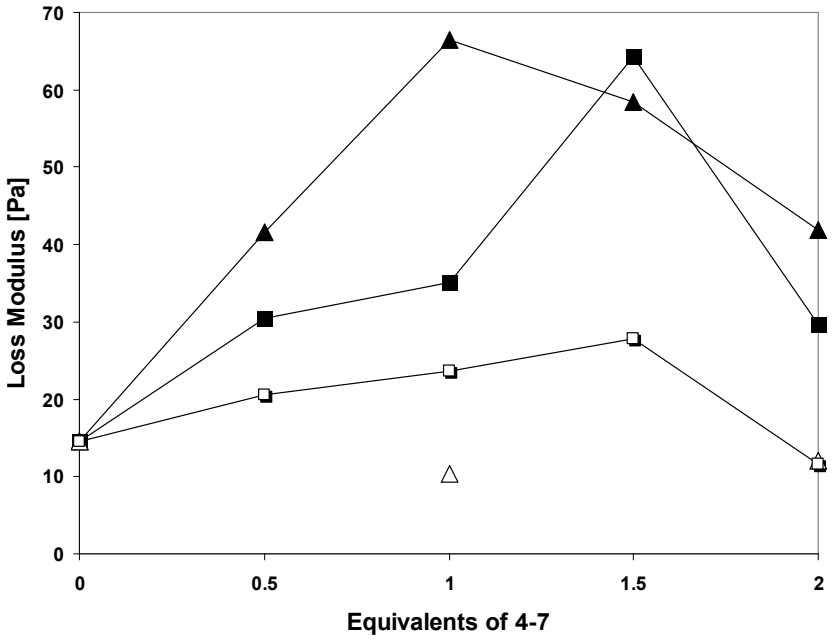


Figure 6.7 Crosslinking profile of **Poly-12** using crosslinking agents (**4**-**7**): **4** (solid triangles), **5** (solid squares), **6** (empty triangles) and **7** (empty squares).

6.7 Thermal reversibility studies

The thermal reversibility studies of **Poly-12-4** and **Poly-12-5** are shown in Figure 6.8, with both networks showing strong temperature dependence. Both samples showed large but gradual decreases in G'' over the temperature range, but no sharp transitions could be observed for either sample, however sharp decrease in the G' values were seen at 60°C for **Poly-12-4** and at 40°C for **Poly-12-5**. In the cooling cycle **Poly-12-5** shows almost quantitative recovery as compared to **Poly-12-4**. The decrease in moduli of the crosslinked systems is much stronger than temperature related changes in viscosity for the pure solvent, from 0.0028 Pa.s to 0.0013 Pa.s over the same temperature range.

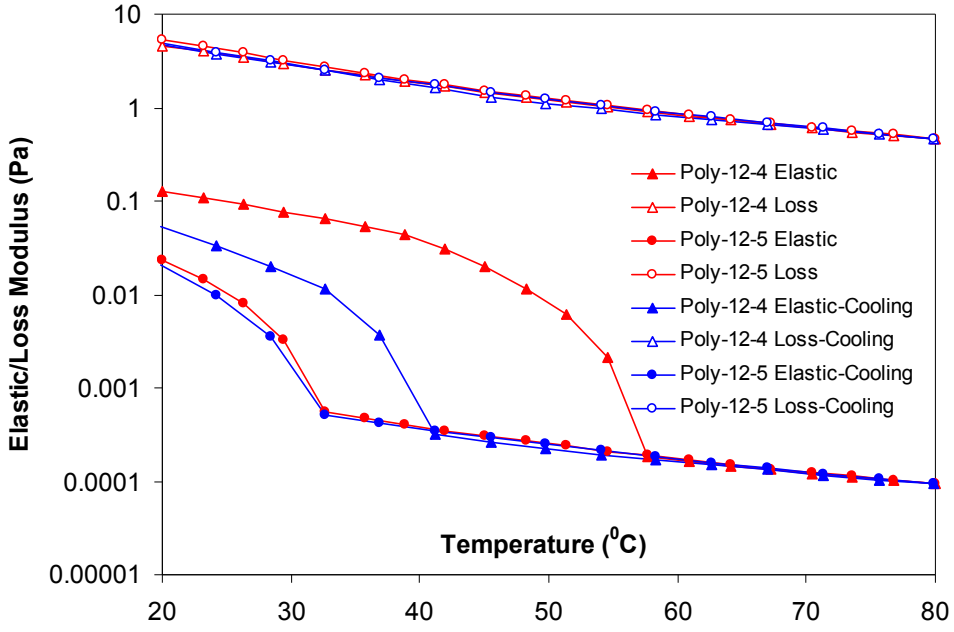


Figure 6.8 Temperature sweep profile: **Poly-12-4** (circles) and Poly-**12-5** (triangles). G' and G'' were measured at $\omega = 6.3$ rad/s. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G'']. The red curves represent the heating profile whereas the blue curves represent the cooling profile.

The degree of crosslinking was also an important parameter that influenced the thermal responsiveness of the networks. Figure 6.9 depicts the heating sweep for **Poly-**

12-5 at 0.5, 1.0, 1.5 and 2.0 equivalents of the crosslinking agent **5** added. It can be seen that as the degree of crosslinking increase from 50 to 150%, the temperature at which decrease in the *G′* values are seen is shifted from around 35 to 50°C. However, at 2.0 equivalents of **5**, the system shows a thermal transition at 35°C similar to that having 0.5 equivalents of **5**. Thus indicating that the network structures are highly dependent upon the concentration of the crosslinking agent.

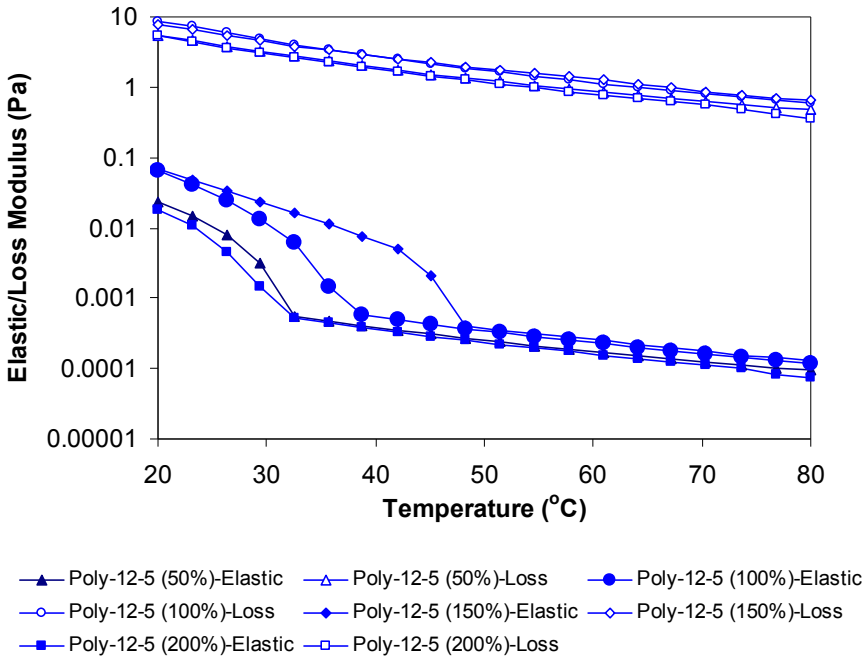


Figure 6.9 Heating profile for **Poly-12-5:** 50% (triangles), 100% (circles), 150% (diamonds) and 200% (rectangles). Filled symbols denote the elastic modulus [*G′*], whereas empty symbols denote the loss modulus [*G″*]. *G'* and *G″* were measured at $\omega =$ 6.3 rad/s. Percentages represent the mol% of crosslinking agent **5**.

6.8 Summary and conclusions

In this chapter, complementary hydrogen bonded polymer networks from random copolymers functionalized with thymine residues via ROMP have been synthesized. It

has been demonstrated that the molecular architecture of the polymer as well as the crosslinking agent have a profound effect on the subsequent network micro-structure, which in turn affects the properties of the resultant material. The change of the cyanuric acid motif to the thymine motif which is incapable of multi-point array formation by hydrogen bonding resulted in networks which were either viscous or free-flowing liquids, no viscoelastic gel was formed as in the case of the cyanuric acid-2,4-diaminotriazine system.

6.9 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 catalyst was purified by filtration using purified benzene under an atmosphere of argon. Spacer monomer **1**[2], thymine monomer **2**[6], cyanuric acid monomer **3**[2], ditopic 2,4-diaminotriazine crosslinking agent **4**[2], Hamilton wedge crosslinking agent **5**[2] and, monotopic 2,4-diaminotriazine **6**[5] were synthesized according to published procedures. The monotopic Hamilton wedge **7** was synthesized as described in Chapter five.

Characterization procedure

As reported in Chapter three.

Polymerizations

The synthesis of the polymer **Poly-12** is described as a representative example: Monomers **1** (1.890 g, 7.56 mmol) and **2** (349.86 mg, 0.84 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 6.91 mg ([M]/[I] = 1000:1) 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 after 6 hours, a drop of ethyl vinyl ether was added to terminate the polymerization, followed by prolonged drying at room temperature under high vacuum for 24 hours to remove all the solvent. The ^{1}H and ^{13}C NMR spectra of all copolymers are analogous to the ones reported in the literature.[6,1]

Crosslinking experiments

The preparation of **Poly-12-4** is described as a representative example: **Poly-12** (176 mg, 0.06 mmol based on thymine groups along the polymer backbone) was dissolved in 1.584 g of 1-chloronaphthalene (10 weight%). Then 18.92 mg (0.06 mmol based on the hydrogen bonding sites allowing for quantitative crosslinking) of **4** was added to the sample and the suspension was heated until a clear homogenous solution was obtained. The viscous liquid was then allowed to rest at room temperature for least twelve hours before rheological measurements were carried out.

Rheological characterization

The rheological testing protocol of all polymer solutions has been described in Chapter five. Flow experiments were carried out for all samples of **Poly-12**, in which the complex viscosity at increasing and decreasing shear rates was measured, the shear rate was varied from 0.01 to 100 s^{-1}.

6.10 References

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CHAPTER SEVEN

Modulating Mechanical Properties of Self-assembled Polymer Networks by Multi-functional Complementary Hydrogen Bonding

7.1 Abstract

Complementary hydrogen bonded polymer networks based on two different hydrogen bonding recognition units namely cyanuric acid and thymine have been synthesized. The cyanuric acid and thymine based terpolymer were crosslinked using multi-functional complementary hydrogen bonding interactions and their network properties studied using rheometry. Two distinct hydrogen bonding motifs were used for the inter-chain crosslinking, three-point hydrogen bonding and six-point hydrogen bonding interactions. The three-point hydrogen bonding complexes were based on cyanuric acid-2,4-diaminotriazine or thymine-2,4-diaminotriazine, whereas the six-point hydrogen bonding complexes were based on cyanuric acid- Hamilton wedge receptor interactions. The terpolymers were crosslinked with the addition of the 6-dodecyl-2,4-diaminotriazine to give a highly viscoelastic solid,. This crosslinked material could be de-crosslinked at room temperature by the addition of mono-functionalized Hamilton wedge receptor agent which displaced the three-point hydrogen bonding complex between the cyanuric acid and the 2,4-diaminotriazine and resulted in functionalization of the cyanuric acid by the formation of the more stable six-point complex formation. Hence by altering the hydrogen bonding recognition unit for inter-chain crosslinking, one could decrosslink a viscoelastic gel to a low viscosity liquid at room temperature. Furthermore the viscoelastic gel could also be re-crosslinked with the di-functional Hamilton

crosslinking agent (directed re-crosslinking), which resulted in the transformation of the viscoelastic gel to a highly viscous liquid at room temperature. Hence by using multi-functional complementary hydrogen bonding interactions the mechanical properties of the self-assembled networks can be modulated at room temperature.

7.2 Introduction

In Chapter 5 it was seen that the cyanuric acid functionalized polymer, could be transformed into either a highly viscoelastic solid, by using 2,4-diaminotriazine functional agents or could be transformed into a highly viscous liquid by crosslinking it with the ditopic wedge crosslinking agent. In stark contrast it was also seen that thymine functionalized polymers always resulted in either free flowing liquids to highly viscous liquids in Chapter six, no matter which crosslinking agent was used to crosslinked the polymer. Furthermore the monotopic Hamilton wedge agent and the monoDAT (6-dodecyl 2,4-diaminotriazine) acted as functional or endcapping agents for cyanuric acid functionalized and thymine functionalized respectively.

In this chapter, the application of using multiple hydrogen bonding interactions to alter crosslinked network architecture which in turn alters the physical properties of the materials will be demonstrated. By using multiple hydrogen bonding interactions, it could be possible to modulate to a large extent the physical property of noncovalent polymer networks, thus paving the way for the study of using multiple noncovalent interactions to probe the structure-property relationship in supramolecular polymers. Furthermore, by using competitive hydrogen bonding interactions one can change the network microstructure of these networks. The change in the micro-structure can result in distinct and significant changes of physical properties of these materials. In particular, a terpolymer-based system in which multiple hydrogen bonding interactions based on cyanuric acid and thymine functional groups which can be used to manipulate and modulate the physical properties of the networks, will be studied. This system is based on complementary hydrogen bonded polymeric network system, in which the hydrogen

bonding interactions between the functional groups attached to the polymer and the crosslinking agent are altered, resulting in formation to distinct materials having different rheological characteristics.

7.3 Research design

The research design for this study is centered around two different hydrogen bonding motifs based on cyanuric acid and thymine. It has been known in the past that the six point hydrogen bonded complexes are more thermodynamically stable than the three point hydrogen bonded complexes.[1-3] In Chapters 5 and 6, it was shown that the difference in interaction strength has profound effects on the mechanical properties of the crosslinked network. Additional control over network structure and physical properties can be obtained by combining multiple crosslinking agents with a single polymer. For example, if the Hamilton wedge receptor is added to the three point hydrogen bonded complex of cyanuric acid and the 2,4-diaminotriazine, it could potentially disrupt the three point hydrogen bonded complex resulting in favor of the formation of more stable six-point hydrogen bonded complexes between cyanuric acid and the Hamilton wedge receptor, as shown in Figure 7.1. This would then result in the disruption of the three-point multi-array network between the cyanuric acid and 2,4-diaminotriazine to form a more loosely connected system consisting of the cyanuric acid-wedge complex.

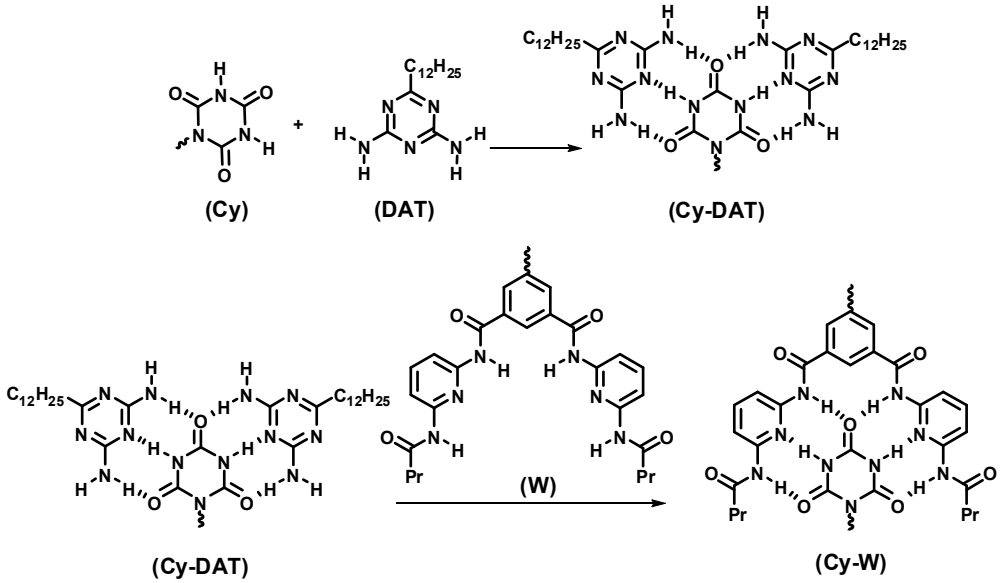


Figure 7.1 Self-assembly motifs: (A) Three point hydrogen bonded complex between cyanuric acid and 2,4-diaminotriazine (Cy-DAT), (B) de-complexation of cyanuric acid-2,4diaminotriazine complex (Cy-DAT) with Hamilton wedge receptor (W) via six point hydrogen bonding to form cyanuric acid-Hamilton wedge complex (Cy-W).

On the other hand, thymine residues possess only a single ADA face, so that it can form complexes with the monotopic 2,4-diaminotrazine crosslinking agent, but not exhibit multi-point array formation. When the Hamilton wedge receptor, which has two 2,6-diaminopyridine centers, is added, thymine can form a 2:1 complex via a three-point hydrogen bonding interaction with Hamilton wedge receptor, leading to effective inter-chain crosslinking and an increase in viscosity. By combining the competitive binding of the crosslinking agents with the functionalized side chains, the aim is to modulate the network micro-structure.

The cyanuric acid and thymine moieties are anchored covalently onto a poly(norbornene) backbone by copolymerizing monomers **1**, **2** and **3** via ROMP. Hydrogen bonded crosslinking was carried out by adding ditopic 2,4-diaminotriazine **4** or ditopic Hamilton wedge receptors **5** to the polymer solution. Monotopic 2,4-

diaminotriazine **6** and monotopic Hamilton wedge receptors **7** were used as the second set of crosslinking agents. All characterizations of the polymer were carried out in 1-chloronaphthalene, which is a non-competitive, high boiling solvent with high solubility for all copolymers. All monomers and crosslinking agents are shown in Figure 7.2.

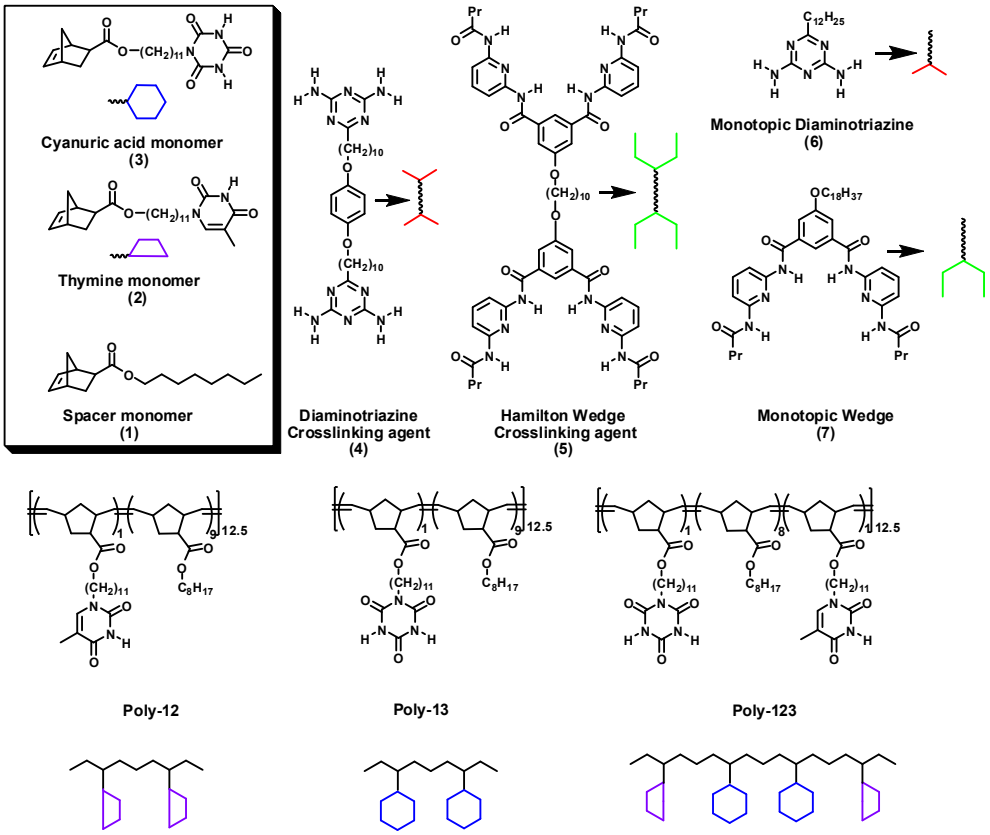


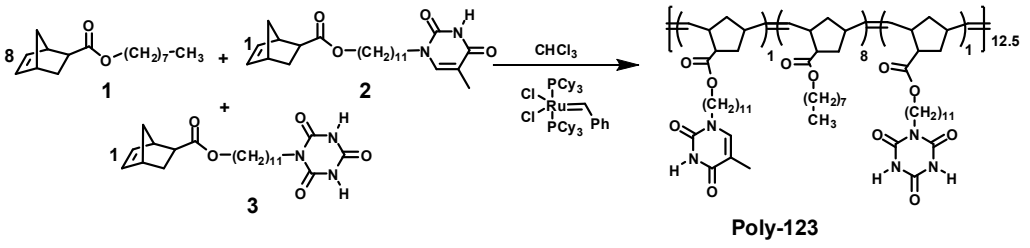
Figure 7.2 Overview of monomers **1-3,** crosslinking agents **4-6,** and polymers **Poly-12, Poly-13** and **Poly-123** used in this study.

7.4 Results and discussions

7.4.1 *Polymerization studies*

The detailed polymerization behavior of monomers **1-3** has been reported previously. [4-6] All monomers can be copolymerized in a statistical manner via ROMP in chloroform at room temperature using Grubbs' first generation initiator (Scheme 7.1).[4-6]

The ROMP copolymerization of these monomers results in polymers with controlled molecular weight and relatively low polydispersities. Table 7.1 lists the results of gel-permeation chromatography characterization. The polymers were designed to possess low concentrations of the monomer **3**, in order to optimize the degree of crosslinking while maintaining good solubility in 1-chloronaphthalene**.** In Chapter 5 it was seen that the solubility of **Poly-13** in 1-chloronaphthalene strongly depends on the mole content of **3** and the degree of polymerization, which could be attributed to self-association of the cyanuric acid groups. In contrast to **Poly-13**, **Poly-12** exhibits very good solubility in 1-chloronaphthalene even at 30 mol % of **2** and at degrees of polymerization as high as 1000. The solubility of terpolymer **Poly-123** was mainly determined by the polymer molecular weight and the mole fraction of monomer **3**. To obtain polymers which were completely soluble in both chloroform and 1-chloronaphthalene (10 wt %) at room temperature, the cyanuric acid and thymine content was kept equal at 10 mol % and the monomer to initiator ratio [M]/[I] was kept at 125 .



Scheme 7.1 Synthesis of **Poly-123** by random polymerization of monomers **1**, **2** and **3** via ROMP.

Table 7.1 GPC data of unfunctionalized terpolymer **Poly-123**. Polymer abbreviations are based on Scheme 7.1.

Entry	[M]/[I]	M_n (10^3)	M_w (10^3)	PDI
Poly-123	125	94.0	65.0	1.4

7.4.2 *Self-assembly studies*

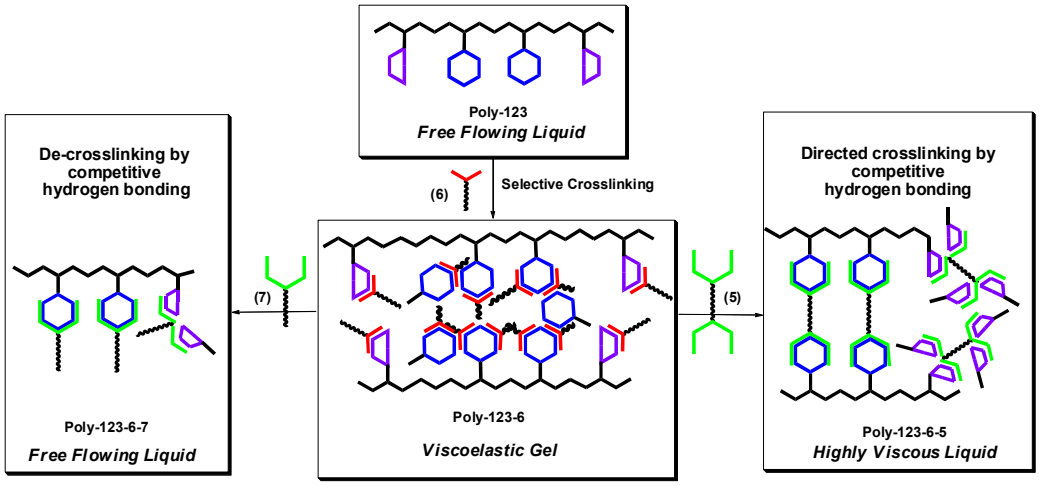
Before conducting crosslinking studies, the competitive hydrogen bonding between monomer **3** and the monotopic compounds **6** and **7** was first investigated. Using ^{1}H NMR spectroscopy, the chemical shifts of the amine proton of **6**, the amide protons of **7** and the imide proton of **3** both before and after self-assembly were monitored. These self-assembly experiments were performed using a 0.2 M solution of the compounds in deuterated chloroform at room temperature and corrected for solvent dilution effects. First the self-assembly of **3** with **6** was studied; upon the addition of two equivalents of **6** to the solution, the imide signal of **3** shifted downfield from 9.78 ppm to 13.81 ppm**,** while the amine proton signals of **6** shifted downfield from 5.33 ppm to 5.74 ppm. Addition of one equivalent of **7** to the mixture resulted in the downfield shifts of the imide protons of **3** to 13.40 ppm and the amine protons of **4** to 5.80 ppm, whereas the amide protons of **7** shifted from 8.64 and 8.14 ppm to 9.07 and 8.61 ppm respectively. Addition of another equivalent of **7** resulted in the imide proton of **3** to shift to 13.27 ppm, whereas the amide proton signals of **7** were shifted to 8.97 and 8.56 ppm respectively, whereas the amine proton signals of **6** were shifted to 5.74 ppm. Control complexation experiments for **7** with **6** and **3** with **7** were also carried out. It can be concluded from the chemical shifts listed in table 7.2 that the addition of **7** to the complex

formed between **3** and **6** results in decomplexation of cyanuric acid-2,4-diaminotriazine multi-point hydrogen bonded complex, as was hypothesized.

Table 7.2 ^{1}H NMR spectroscopy shifts of small molecule compounds upon hydrogen bonded self-assembly. Symbols: *c* represents the imide protons of **3**, *d* represents amine protons of **6** and *w* represents the amide protons of **7**.

Entry	**^{1}H NMR shifts (ppm)**	**Entry**	**^{1}H NMR shifts (ppm)**
3	9.78^{c}	**7** + 2 Eq. **6**	8.74^{w} & 8.26^{w}, 5.66^{d}
6	5.33^{d}	**3** + 2 Eq. **6**	13.81^{c}, 5.74^{d}
7	8.64^{w} & 8.14^{w}	(**3** + 2 Eq. **6**) +**7**	13.40^{c}, 5.80^{d}, 9.07^{w} & 8.61^{w}
3 + **7**	13.24^{c}, 9.46^{w} & 9.03^{w}	(**3** + 2 Eq. **6**) + 2 Eq. **7**	13.27^{c}, 5.74^{d}, 8.97 & 8.56^{w}

After conducting these preliminary self-assembly studies on monomers in solution, the competitive binding of terpolymer **Poly-123** with multiple hydrogen bonding crosslinking agents was investigated. By applying the strategy of competitive complexation and decomplexation to polymer systems, the network micro-structures of complementary hydrogen bonded networks can be manipulated without the need for synthesizing new polymer materials, as shown in Scheme 7.2.



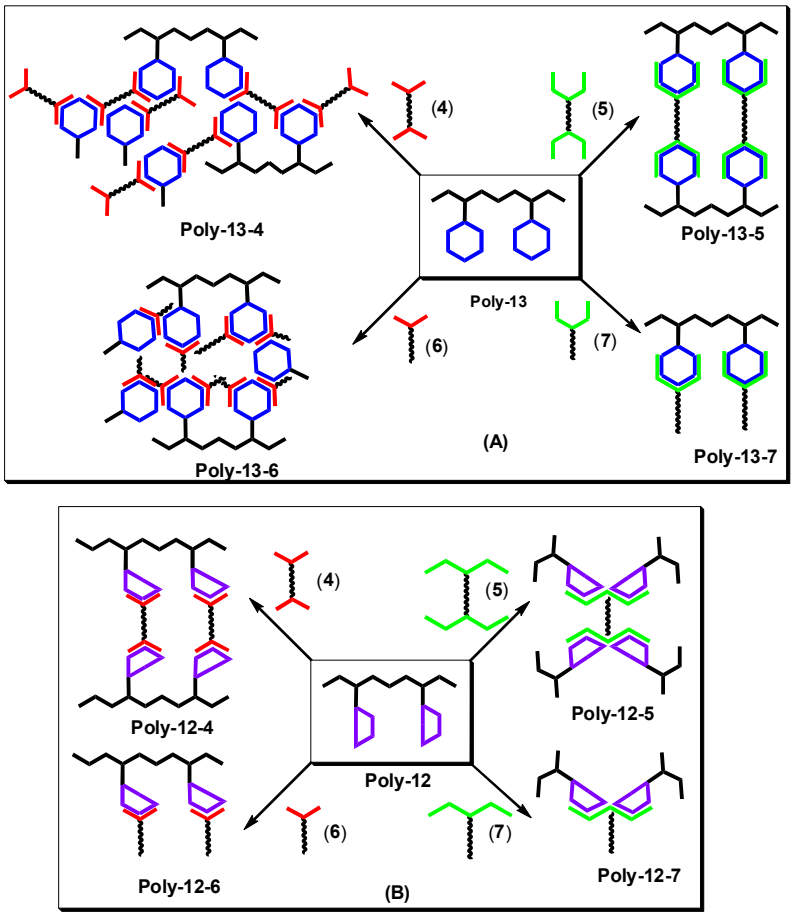
Scheme 7.2 Noncovalent crosslinking and de-crosslinking strategies of **Poly-123**. (A) Selective crosslinking of **Poly-123** using **6**, to give network **Poly-123-6**, (B) de-crosslinking of **Poly-123-6** using **7** to give **Poly-123-6-7** and (C) directed re-crosslinking of **Poly-123-6** using **5** to give **Poly-123-6-5**.

7.5 Crosslinking studies

Complementary hydrogen bonding networks based on **Poly-13**: Cyanuric acid residues are capable of multiple hydrogen bond formation in two distinct ways. Since the cyanuric acid residues have two ADA faces, it can form multi-point hydrogen bonded complex with 2, 4-diaminotriazine moieties, via three and two point hydrogen bonding interactions. The addition of both the ditopic DAT **4** and the monotopic DAT **6** to solutions of **Poly-13** result in strong viscoelastic gels. Somewhat surprisingly. it was found that monotopic DAT **6** resulted in stronger gels (higher values of loss modulus *G′*) than analogous additions of ditopic DAT **4**. This difference can be explained on the basis of steric hindrance: because ditopic DAT **4** has two 2,4-diaminotriazine functional groups attached to a long alkyl linker, steric constraints are imposed on in the formation of the network array. On the other hand, **6** has only one dodecyl alkyl tail, which would result in lower steric hindrance in the formation of the multi-point network structure with the

cyanuric acid groups. As a result network formed by **6** are more tightly packed as compared to those formed by **4**. To test this hypothesis, 1,3,5-triazine-2,4-diamine was added to crosslink **Poly-13** under the same conditions. 1,3,5-triazine-2,4-diamine has a very similar structure to **6**, but without the alkyl chain. It was found that 1,3,5-triazine-2,4-diamine was indeed a very efficient crosslinking agent and resulted in very stiff gels which could not even be loaded into the rheometer for quantitative measurement of the dynamic moduli. This control experiment proves that the presence of an alkyl tail at the 6 position of the triazine ring hinders the formation of an array network structure with the cyanuric acid groups.

The cyanuric acid residues can also form a 1:1 complex via the stronger six-point hydrogen bonding interaction with the Hamilton wedge receptor. The resulting cyanuric acid - Hamilton wedge receptor complex has been utilized extensively in supramolecular science because of its high association constant (10^6 M^{-1}) in chloroform.[4,2] Chapter 5 discussed the addition of the wedge crosslinking agent **5** to **Poly-13**, which resulted in polymer networks **Poly-13-5** with strong point to point linkages, but with lower intermolecular network connectivity. The crosslinked system was a highly viscous liquid as opposed to the strong viscoelastic gels obtained by the addition of 2,4-diaminotriazine based crosslinking agents. The monotopic wedge **7** acts as an endcapping agent for **Poly-13**, and hence **Poly-13-7** is an uncrosslinked low-viscosity liquid in which the cyanuric acid groups are functionalized by the wedge recognition unit (Scheme 7.3).



Scheme 7.3 Cartoon representation of the microstructures of networks based on (**A**) **Poly-13**: **Poly-13-4**, **Poly-13-5**, **Poly-13-6**, **Poly-13-7** and (**B**) **Poly-12**: **Poly-12-4**, **Poly-12-5**, **Poly-12-6**, **Poly-12-7**.

Complementary hydrogen bonding networks based on **Poly-12**: Unlike the cyanuric acid residues, thymine recognition units are capable of only three-point hydrogen bonding interactions. As seen in Chapter six, unlike the cyanuric acid residues thymine has just one ADA face which can take part hydrogen bonding interactions. This important structural difference resulted in a drastic difference in mechanical properties between networks based on **Poly-12** and **Poly-13**. As discussed in detail in Chapter 6, the addition of ditopic DAT **4** to **Poly-12** resulted in the formation of viscous liquids, while the addition of monotopic **6** did not enhance the viscosity significantly, in stark contrast

to the highly viscoelastic network **Poly-13-6**. This observation can be explained by the fact that monotopic DAT **6** acts as an endcapping agent for the thymine groups and can therefore not create inter-chain crosslinks (Scheme 7.3). Ditopic wedge **5** and monotopic wedge **7** have four and two 2, 4-diaminopyridine functional groups, respectively. Hence **5** can act as a tetra-topic crosslinking agent, whereas **7** simple acts as a ditopic crosslinking agent for **Poly-12**. It was found that the addition of both crosslinking agents resulted in increases of the viscosity of the polymer solution, but no viscoelastic gel formation was observed. As expected, the addition of tetra-topical **5** resulted in greater increase in the solution viscosity than that of di-topic **7**.

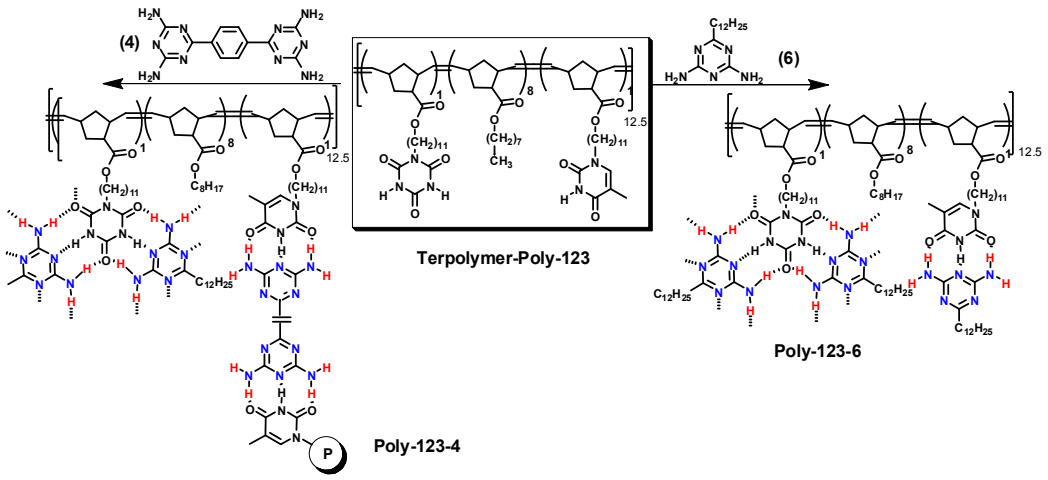
In conclusion, the experiments show that **Poly-12** and **Poly-13** form complementary networks with vastly different physical properties, depending upon the type of crosslinking agent used. Copolymerization of monomers **2** and **3** yielding **Poly-123** should therefore create a polymer scaffold that combines the crosslinking characteristics of thymine and cyanuric acid residues. By carefully choosing the crosslinking agent used for inter-chain crosslinking of **Poly-123** and tuning its concentration, one should be able to manipulate the network microstructure. Table 7.3 summarizes the results for copolymer crosslinking and illustrates that the combination of different functional groups crosslinking agent represents a versatile toolkit for modulating physical properties of polymer networks based on complementary hydrogen bonding interactions.

Table 7.3 Toolkit for hydrogen bonding interactions. *a* represents *G′/ G″* and *b* represents |*G**| values (in Pa) for crosslinked polymers of **Poly-12** and **Poly-13**, at frequency of 1 Hz (6.28 rad/s). strain 0.1 and at 25°C.

Polymer	Poly-12	Poly-13	Poly-123
DAT (4)	**Liquid** [0.04^a, 35.0^b]	**Viscoelastic Gel** [0.95^a, 527^b]	***Poor Gelation***
Wedge (5)	**Liquid** [0.06^a, 67.0^b]	**Viscous Liquid** [0.28^a, 2990^b]	***Highly Viscous Liquid***
MonoDAT (6)	**Liquid** [$<0.01^a$, 10.4^b]	**Viscoelastic Gel** [4.6^a, 129435^b]	***Viscoelastic Gel***
MonoWedge (7)	**Liquid** [0.04^a, 23.6^b]	**Liquid** [$<0.01^a$, 2.7^b]	***Liquid***

7.5.1 *Selective Crosslinking of Poly-123*

From the studies on copolymers **Poly-12** (Chapter 6) and **Poly-13** (Chapter 5) it has been established that only interactions between cyanuric acid and 2,4-diaminotriazine resulted in viscoelastic gels. When the ditopic crosslinking agent **4** was added to **Poly-123**, simultaneous crosslinking of the thymine and the cyanuric acid side chains is expected. Because the crosslinking of the thymine groups results in the formation of viscous liquids, competing with the formation of solid gels with cyanuric acid, **4** is a poor choice as selective crosslinking agent for **Poly-123**.



Scheme 7.4 Noncovalent crosslinking of **Poly-123**. (A) Selective crosslinking of **Poly-123** using **6**, to give network **Poly-123-6**, (B) Non selective crosslinking of **Poly-123** using **4**.

In contrast, the addition of monotopic DAT **6** to **Poly-123**, should result in two distinct types of hydrogen bonded complexes: *(i)* three point thymine-**6** complex formation, which acts as endcap for the thymine functionalized groups, and *(ii)* multi-point hydrogen bonding of cyanuric acid residues-**6**, resulting in inter-chain crosslinking into a highly viscoelastic array network (Scheme 7.4). To probe the effects of competitive binding on the gel formation, the amount of **6** added to **Poly-123** was varied between 0 and 2 equivalents of **6**, as defined with respect to combined number of thymine and cyanuric acid residues in solution. The results of these crosslinking experiments are shown in Figure 7.3. It was found that 0.5 equivalent of **6** leads to the formation of a highly viscoelastic gel, whereas at lower concentrations of **6** viscous liquids are formed due to lack of connectivity. This behavior is analogous to the crosslinking profile of copolymer **Poly-13** with **4** in Chapter 5. More surprisingly, however, is that increasing the amount of **6** above 0.5 equivalent causes decrease in the G', to the point were another crossover between G' and G'' is observed, indicating break-up of the network into a

highly viscous liquid. The likely explanation for this phenomenon is that functionalization of thymine residues leads to steric hindrance of the array formation between crosslinking agent and cyanuric acid residues.

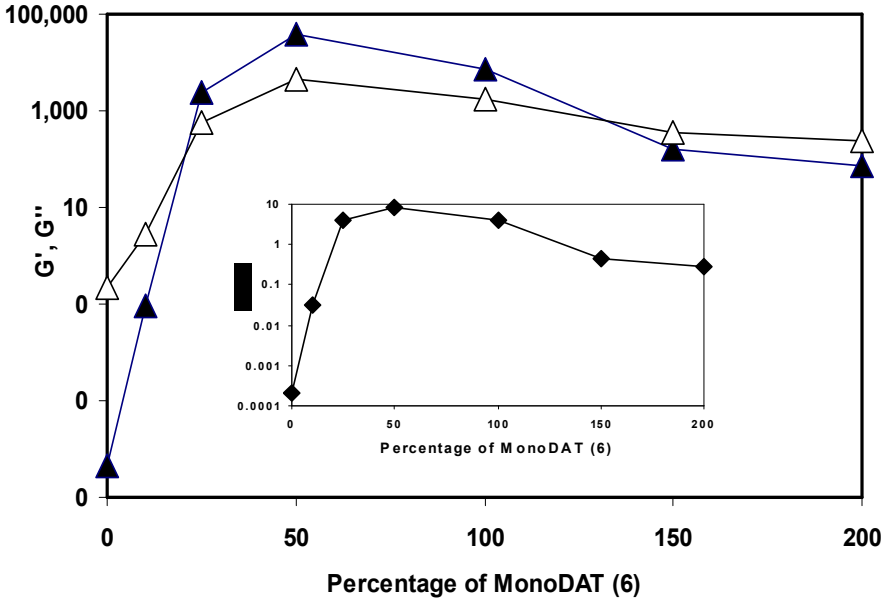
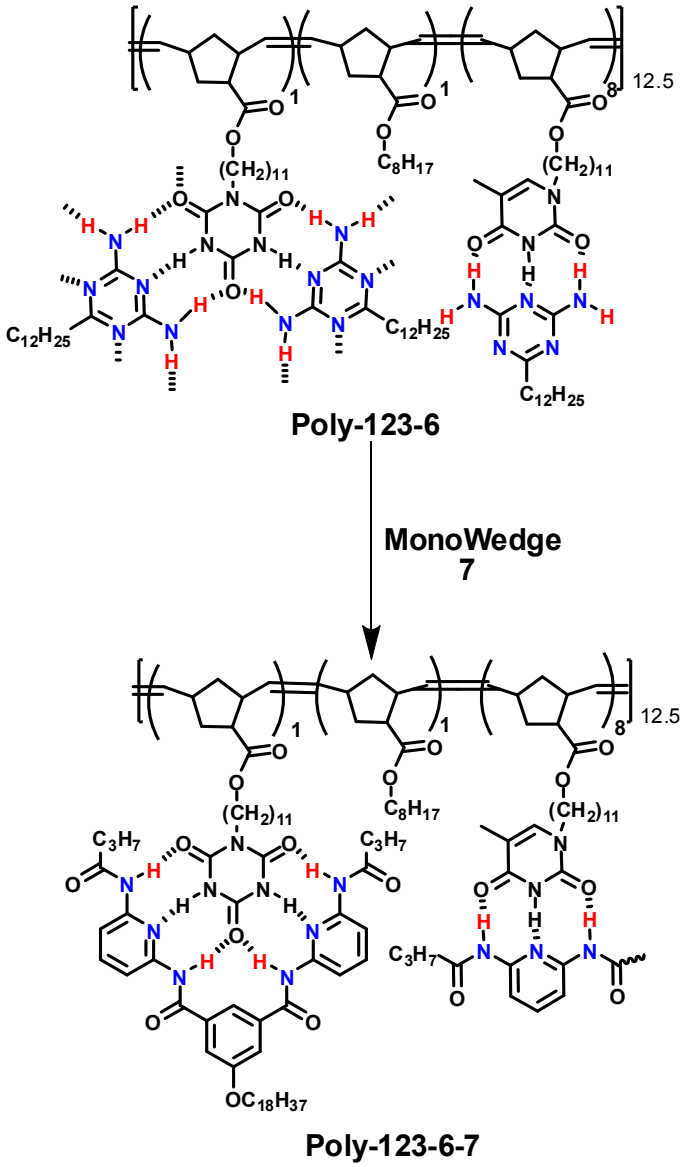


Figure 7.3 Crosslinking profile of **Poly-123** using **6**. Filled symbols denote the elastic modulus [*G′*], whereas empty symbols denote the loss modulus [*G″*] at strain value of 0.1 and angular frequency of 6.28 rad/s. The inset represents the ratio *G′*/*G″* as a function of the amount of **6** added. The percentage of **6** is based on the molar ratio to combined cyanuric acid and thymine groups attached to the polymer.

7.5.2 *Room temperature decrosslinking of Poly-123-6 using competitive hydrogen bonding interactions*

After having studied the crosslinking profile of **Poly-123** with **6**, the multi-point hydrogen bonded array of cyanuric acid-2,4-diaminotriazine was disrupted by the addition of monotopic wedge agent **7**, which has been found to act as an efficient endcapping agent for cyanuric acid residues and as a weak crosslinking agent for thymine residues in copolymer systems. Based on the monomer studies presented above, the

addition of **7** to the terpolymer is anticipated to break-up relatively weak three-point complexes between cyanuric acid and **6**, in favor of the formation of significantly stronger six point hydrogen bonded complexes between cyanuric acid and **7** (Scheme 7.5). The results are presented in Figure 7.4 for a terpolymer system that was initially crosslinked with 1.0 equivalent of **6**, before adding the monotopic wedge **7**.



Scheme 7.5 Noncovalent de-crosslinking strategy of **Poly-123-6** using **7** to give **Poly-123-6-7**.

Even though **7** acts as a weak crosslinking agent for the thymine functional groups, the addition of **7** does not result in effective inter-chain multipoint crosslinking, as was shown in Chapter 6 and Table 7.3. Therefore addition of **7** predominantly breaks up the multi-point array network of the cyanuric acid side chains and **6**, which causes a dramatic decrease in the G' values and a clear change from an elastic gel to a low viscosity liquid. The addition of 0.4 equivalents of **7** induces a crossover of G'' and G' values, which represents this gel-to-liquid transition.

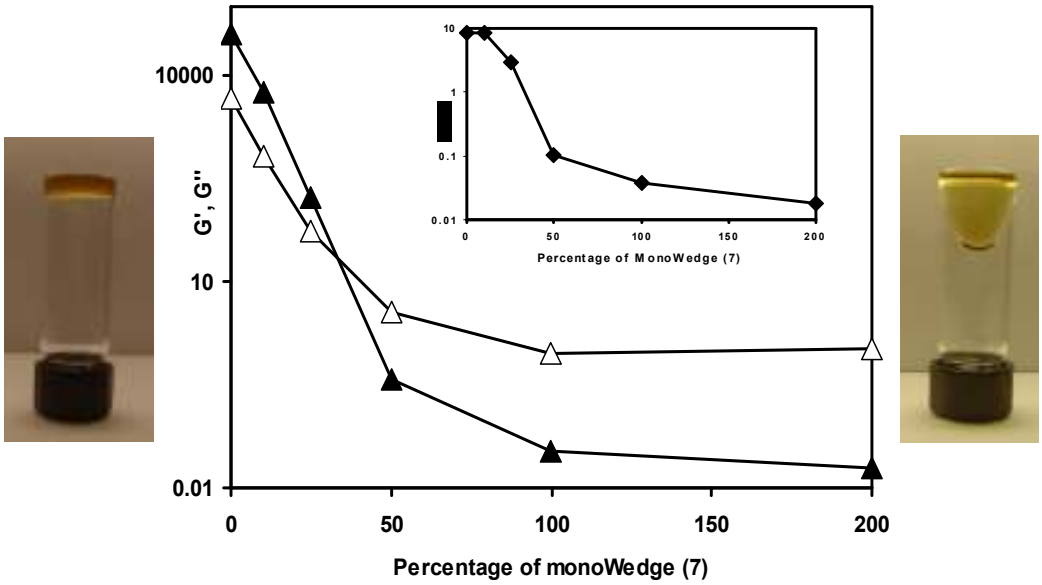
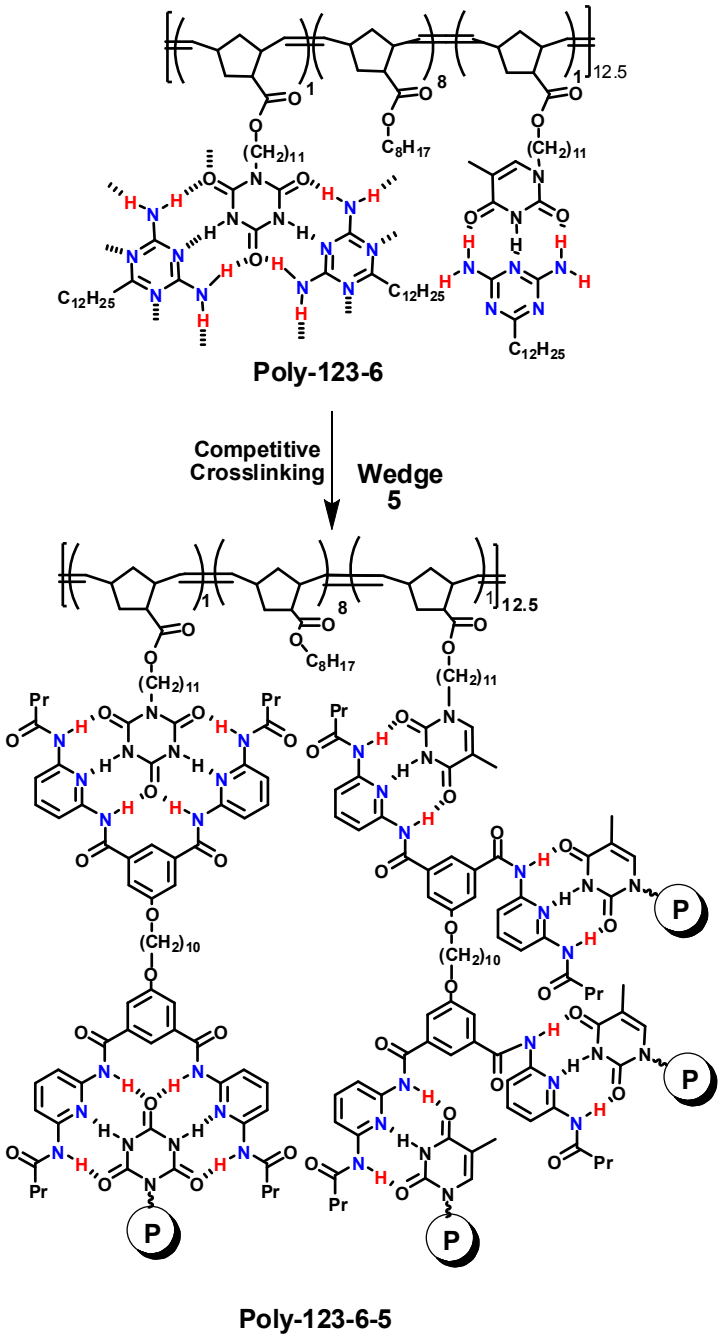


Figure 7.4 Room temperature decrosslinking profile of **Poly-123-6** using **7**. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at strain value of 0.1 and angular frequency 6.28 rad/s. Inset represents the ratio G'/G'' as a function of the amount of monoWedge added. The percentage of **7** is based on the molar ratio to combined cyanuric acid and thymine groups attached to the polymer. Optical micrographs of inverted vials 3-4 hours after vial inversion with (left) the stable elastic gel **Poly-123-6**, (right) the de-crosslinked liquid **Poly-123-6-7**. All polymers and additives were dissolved in 1-chloronaphthalene.

7.5.3 *Directed re-crosslinking of Poly-123-6 via competitive hydrogen bonding interactions*

The addition of monotopic agent **7** to **Poly-123-6**, resulted in gel break-up, due to the fact that addition of **7** causes strong endcapping of the cyanuric acid residues. Analogously, the addition of the ditopic Hamilton wedge crosslinking agent **5** would be expected to disrupt the strong crosslinking of the cyanuric acid residues as well. Since **5** is not an endcapping agent and will still give rise to crosslinking when it competitively displaces **6**. However, Table 7.3 and Chapter 5 clearly showed that the network microstructures due to crosslinking of the cyanuric acid residues with 2,4-diaminotriazine based **6** and Hamilton wedge crosslinking agent **5** are markedly different.



Scheme 7.6 Noncovalent directed re-crosslinking of **Poly-123-6** using **5** to give **Poly-123-6-5**. The network structure depicts the crosslinking of the thymine residues by **5**.

The addition of **6** causes multi-point inter-chain hydrogen bonding interactions leading to a three dimensional network structure, whereas the addition of **5** results in strong albeit two-point linkages. Hence by the addition of **5** to crosslinked terpolymer

Poly-123-6, the network microstructure might be tuned between a three dimensional multipoint array-like network structure to a network structure predominantly linked by strong two-point linkages. Due to the dynamic nature of the hydrogen bonding interactions, the addition of **5** (which can act as a tetrafunctional crosslinking agent for the thymine residues as depicted in Scheme 7.3), can crosslink the thymine residues. However, as indicated in Table 7.3, the crosslinking of thymine residues by **5** does not lead to effective multipoint inter-chain crosslinking and it is expected that these crosslinks would contribute minimally to *G′*. Hence the addition of **5** is expected to lead to an increase in *G″* values. The rheological characteristics of directed re-crosslinking studies by adding variable amounts of **5** to a crosslinked **Poly-123-6** (1.0 equivalent of **6** initially) are shown in Figure 7.5. Optical micrographs of the elastic gel **Poly-123-6** (vial A) and the re-crosslinked viscous liquid (1 eq. of **5**) **Poly-123-6-5** (vial B) are shown in Figure 7.6.

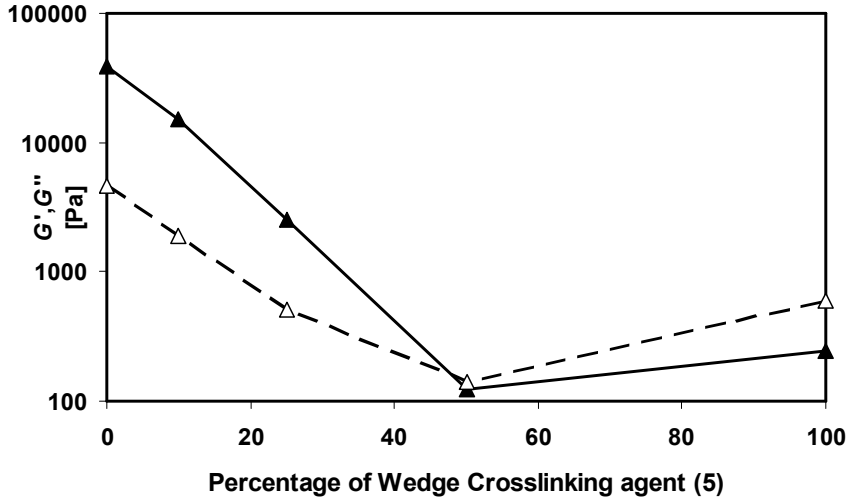


Figure 7.5 Directed re-crosslinking profile of **Poly-123-6** using (**5**). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at strain value of 0.1. The percentage of **5** is based on the molar ratio to combined cyanuric acid and thymine groups attached to the polymer.

It can be seen from both the rheological data and the images that **Poly-123-6** does not flow whereas **Poly-123-6-5** exhibits viscous behavior.

(A) **(B)**

Figure 7.6 Optical micrograph of inverted vials 1-2 hours after vial inversion with (left) the sTable elastic gel **Poly-123-6**, (right) the re-crosslinked viscous liquid **Poly-123-6-5 (**1 eq. of **5)**. All polymers and additives were dissolved in 1-chloronaphthalene.

Frequency sweeps of **Poly-123** (low-viscosity liquid), **Poly-123-6** (viscoelastic solid), **Poly-123-6-5** (viscous liquid) and **Poly-123-6-7** (low viscosity liquid) are presented in Figure 7.7 to provide more detailed insight into the rheology of the samples. These frequency sweeps further support the notion that by using multi-functional complementary hydrogen bonding interactions it is possible to tune the materials properties of samples originating from a single parent polymer backbone.

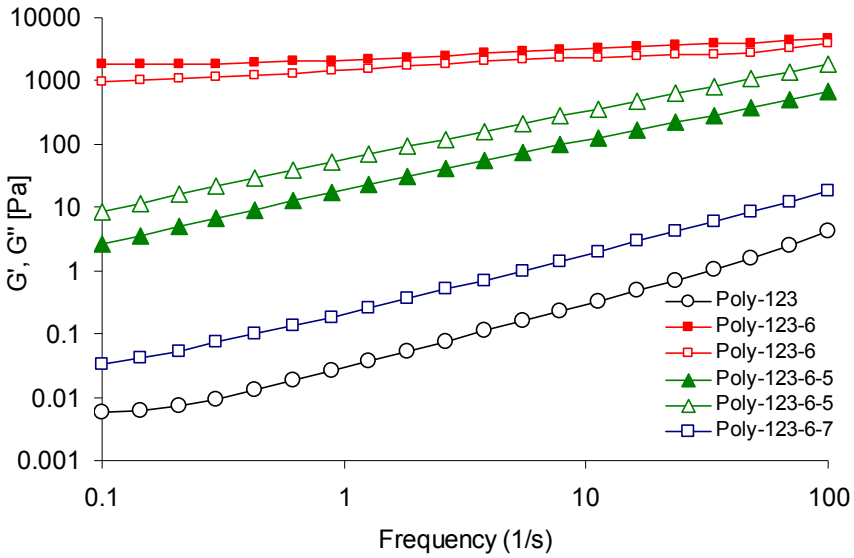


Figure 7.7 Frequency sweeps at 20°C at strain amplitude 0.1: (A) **Poly-123** (circles), (B) **Poly-123-6-7** (rectangles), (C) **Poly-123-6-5** (triangles) and (D) **Poly-123-6** (squares). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G'']. G' data for **Poly-123** and **Poly-123-6-7** has been omitted due to very low magnitude.

7.6 Summary and conclusions

In this chapter multi-functional complementary hydrogen bonding interactions have been successfully utilized in changing the network micro-structure of the hydrogen bonded crosslinked polymers. By varying the hydrogen bonding motif used for inter-chain crosslinking, the properties of a single network could be tailored from a viscoelastic solid to a highly viscous liquid to a free-flowing liquid. The ability of altering the physical property of a material by varying the recognition moiety responsible for inter-chain crosslinking allows for tailoring the materials property at room temperature without the need for temperature gradients typical for conventional mono-functionalized hydrogen bonded systems. Such a strategy combines for the first time "Supramolecular

Polymer Chemistry" and polymer "Structure Property Relationship", allowing for further development of tailor-made and highly responsive materials for advanced applications.

7.7 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 catalyst was purified by filtration using purified benzene under an atmosphere of argon. Spacer monomer **1**[6], thymine monomer **2**[4], cyanuric acid monomer **3**[6], monotopic 2,4-diaminotriazine **4**[7], ditopic Hamilton wedge crosslinking agent **5**[6], monotopic Hamilton wedge **6**[8] were synthesized according to published procedures.

Characterization procedure

As reported in Chapter three.

Polymerizations

The synthesis of terpolymer **Poly-123** is described as a representative example: Monomers **1** (1.80 g, 7.2 mmol), **2** (562 mg, 1.34 mmol) and **3** (188 mg, 0.44 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 7.40 mg ([M]/[I] = 1000:1) of the initiator was added to the monomer solution. The solution was stirred at 40°C 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 60°C to remove all the solvent.

The ^{1}H and ^{13}C NMR spectra of all copolymers are analogous to the ones reported in the literature.[4]

Crosslinking experiments

The preparation of **Poly-123-4** is described as a representative example: **Poly-123** (170 mg, 0.12 mmol based on the hydrogen bonding functional groups along the polymer backbone) was dissolved in 1.53 g of 1-chloronaphthalene (10 weight%). Then 36 mg (0.12 mmol based on the hydrogen bonding sites allowing for quantitative crosslinking) of **4** was added to the sample and the suspension was heated until a clear homogenous solution was obtained. The polymer solution was then allowed to rest at room temperature for least twelve hours before rheological measurements were carried out.

Rheological characterization

The rheological testing protocol of all polymer solutions has been described in Chapter five.

7.8 References

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CHAPTER EIGHT

Metal Crosslinked Polymer Networks

8.1 Abstract

Random side-chain functionalized copolymers with SCS palladated-pincer complexes have been synthesized using ROMP. These Pd SCS pincer side-chain functionalized polymers were then subsequently crosslinked via metal coordination interactions using bis-pyridine as the crosslinking agent. Extensive crosslinking via metal coordination was observed which resulted in materials displaying properties varying from being viscoelastic gels to highly viscous liquids. The network properties strongly depended on the extent of crosslinking and the concentration of the polymer in the solution. By varying the SCS palladated pincer loading and by varying the concentration of the polymer, the final network properties of the metal coordinated crosslinked materials can be tuned and controlled.

8.2 Introduction

In Chapters one and two the importance of metal coordination in reversible crosslinking of polymers was explained in detail. In this chapter, the network properties of metal crosslinked polymers based on SCS Pd-pincer complexes will be presented and discussed. Palladated sulfur–carbon–sulfur (SCS) pincer complexes are tridentate, square planar coordination spheres that are particularly useful in molecular recognition because they possess only one coordination site accessible for self-assembly.[1] The aim of this study is to understand the effect of SCS Pd-pincer concentration and the effect of the polymer concentration in the solution on the ability of the system to form viscoelastic gels. Such a study will be helpful in optimizing the molecular architecture for subsequent experiments that will combine metal coordination with hydrogen bonding interactions to yield a multi-functionalized polymer system crosslinked via multiple noncovalent interactions to form a multi-responsive material, as will be shown in Chapter nine.

8.3 Research design

Our research design consists of random copolymers functionalized with SCS palladated pincer complexes as metal coordination sites. The noncovalent functionalization of SCS palladated pincer systems with nitriles, pyridines and phosphines has been studied before.[1-5] The metal coordination motif that is used for inter-chain crosslinking in this study is shown in Figure 8.1.

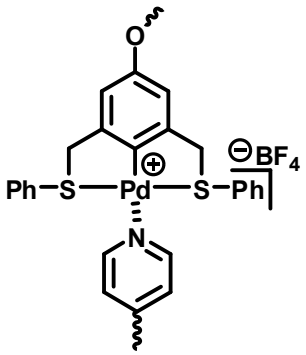


Figure 8.1 Self-assembly motif employed in this study based on SCS-Pd pincer- pyridine complex.

The monomers and the crosslinking agent used in this study are depicted in Figure 8.2. In this study the SCS palladated pincer groups are anchored covalently onto a poly(norbornene) backbone by copolymerizing **1** with **2** using ROMP, to form **Poly-12**. As explained in Chapter 5, monomer **1** serves as a diluent and increases solubility of the polymer in non-polar solvents. Metal coordinated crosslinking was carried by adding bis-pyridine. As described in Chapter 5, all crosslinking processes as well as all characterizations of the resulting crosslinked polymer networks were carried out in 1-chloronaphthalene, a non-competitive, high boiling solvent in which all copolymers have good solubility.

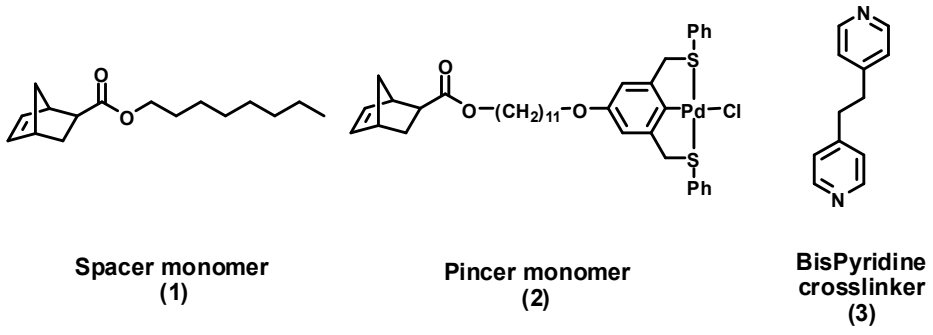
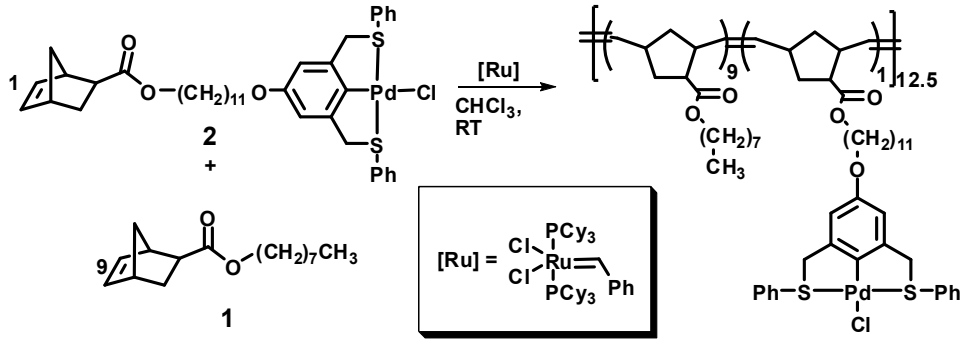


Figure 8.2 Monomers **1-2**, crosslinking agents **3** utilized in this study.

8.4 Results and discussions

8.4.1 *Polymerization studies*

The detailed polymerization behaviors of monomer **1** and **2** have been previously reported. The monomers can be copolymerized in a statistical manner via ROMP in chloroform at room temperature using Grubbs' first generation initiator (Scheme 8.1).[6,3] The ROMP copolymerization of these monomers resulted in polymers with controlled molecular weights and relatively low polydispersities. The polymer composition and molecular weight were found to be important parameters affecting the subsequent syntheses of homogenous crosslinked polymer networks in 1-chloronaphthalene. The polymers were designed to possess low concentrations of the pincer monomer **2** (5-20 mol%), in order to study crosslinking while simultaneously maintaining good solubility in 1-chloronaphthalene**.** The weight average molecular weight was approximately 36000 and number average molecular weight was approximately 29 000 (M_w ~ 35 000, M_n ~ 29 000, PDI = 1.2).

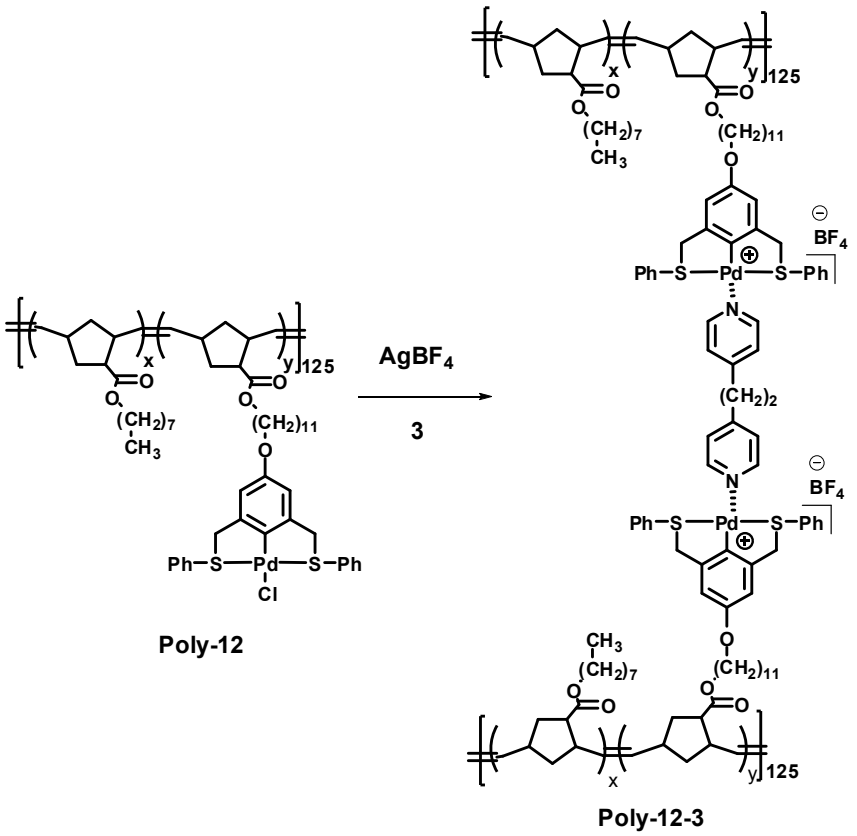


Scheme 8.1 Synthesis of **Poly-12** by random polymerization of monomers **1** and **2**.

8.4.2 *Crosslinking studies*

The detailed self-assembly involving metal coordination of the SCS-Pd pincer centers with pyridine has been explained in Chapters 1-3.[1-3,5] After studying in detail the self-assembly of **Poly-12**, the polymer scaffold was reversibly crosslinked via metal

coordination using crosslinking agent **3**. The crosslinking of **Poly-12** was carried out in two steps, first requiring the activation of Pd centers with silver tetrafluoroborate and then the subsequent coordination of the Pd center with the pyridine. The network structures of **Poly-12-3** are depicted in Scheme 8.2.



Scheme 8.2 Metal coordinated crosslinking of **Poly-12** using crosslinking agent **3** to form **Poly-12-3**.

8.4.3 *Crosslinking behavior of Poly-12-3*

In order to probe effect of important parameters such as concentration of the pincer complex and polymer content of the solution on the ability of the system to undergo gelation, three different crosslinked polymers systems at 100% crosslinking

composition with **3** were studied, (i) **Poly-12-3** (5 mol%-20% SC) which consists of **Poly-12** functionalized with 5 mol% of pincer complex with polymer content in solution being 20 weight% (or solid content SC), (ii) **Poly-12-3** (10 mol%-10% SC) which consists of **Poly-12** functionalized with 10mol% of pincer complex with polymer content in solution being 10 weight% (or solid content SC) and (iii) **Poly-12-3** (20 mol%-10% SC) which consists of **Poly-12** functionalized with 20 mol% of pincer complex with polymer content in solution being 10 weight% (or solid content SC).

It was seen that the even at 100% crosslinked composition and at a relatively higher polymer content **Poly-12-3** (5 mol%-20% SC) was a viscous liquid and not a gel. The other two samples visibly appeared to be viscoelastic solids with **Poly-12-3** (20 mol%-10% SC) being stiffer than **Poly-12-3** (10 mol%-10% SC). In order to gain quantitative analysis, the samples were analyzed using rheology. The amplitude sweep of the above samples is shown in Figure 8.3, from which it can be clearly seen that for **Poly-12-3** (5 mol%-20% SC) $G' < G''$, whereas for the other two samples $G' > G''$, exhibiting a visoelastic nature. **Poly-12-3** (20 mol%-10% SC) exhibited higher moduli than **Poly-12-3** (10 mol%-10% SC) and also more brittle, displaying failure at high strain amplitudes.

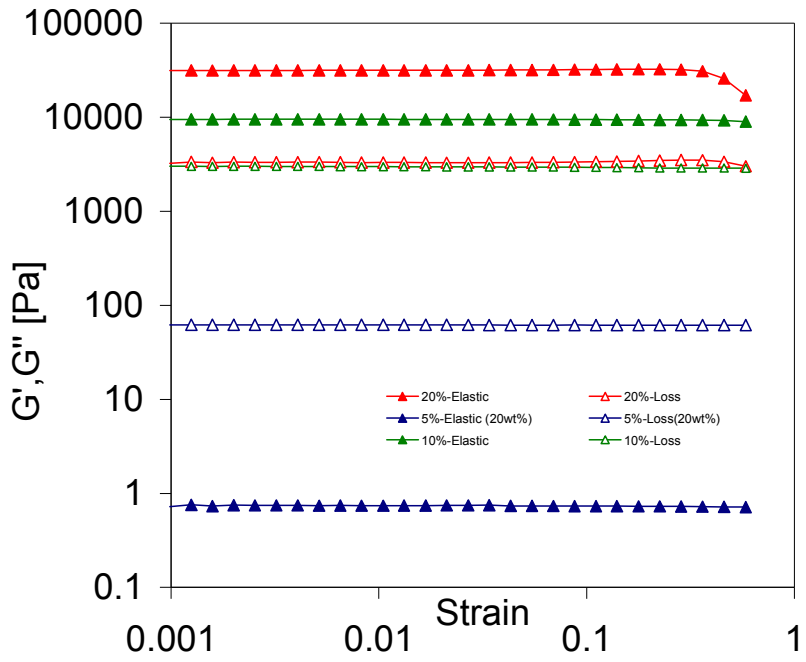


Figure 8.3 Strain amplitude sweep at 20°C at $\omega = 6.3$ rad/s for **Poly-12-3** (5 mol%-20% SC) (triangles), **Poly-12-3** (10 mol%-10% SC) (triangles) and **Poly-12-3** (20 mol%-10% SC) (circles). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''].

The frequency sweeps profiles of the same samples at room temperature are shown in Figure 8.4, from which it can be observed that **Poly-12-3** (20 mol%-10% SC) behaves a typical viscous liquid whereas the other two samples exhibit viscoelastic behavior.

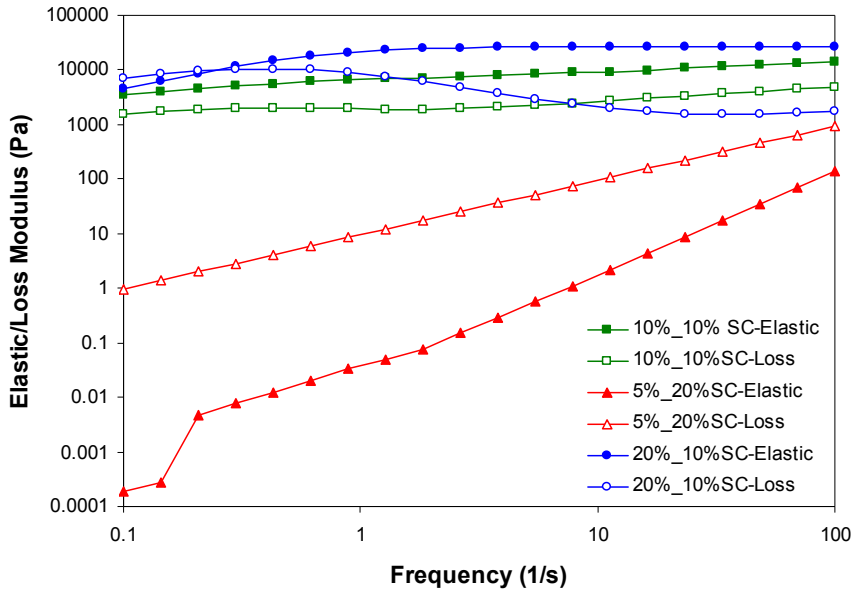


Figure 8.4 Frequency sweep profile at strain amplitude 0.1 and 20°C: **Poly-12-3** (5 mol%-20% SC) (triangles), **Poly-12-3** (10 mol%-10% SC) (squares), **Poly-12-3** (20 mol%-10% SC) (circles). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''].

Interestingly, the low-frequency crossover for the stronger gel, **Poly-12-3** (20 mol%-10% SC), occurs at higher frequencies than the weaker **Poly-12-3** (10 mol%-10% SC). Clearly, the pincer content and the polymer concentration in the solution are both important parameters that affect the ability of the system to gel to form viscoelastic gels: a low functional loading results in viscous liquids even at high polymer concentrations whereas at high functional loadings networks having high modulii are obtained that exhibit fracture at higher strain amplitudes.

8.5 Summary and conclusions

In this chapter, random copolymers functionalized with SCS Pd pincer via ROMP have been synthesized which have been reversibly crosslinked via metal coordination using bis-pyridine as the crosslinking agent. The metal content of the polymer as well as

the polymer content in the solution determine the ability of the system to form viscoelastic gels. It was seen that a metal content of 10 mol% and a polymer content of 10 weight% in 1-chloronaphthalene at 100% crosslinked composition using bis-pyridine as the crosslinking agent, yielded viscoelastic gels which could be easily handled and analyzed. Higher metal loading at the same polymer content yielded in very stiff gels, while lower metal loadings did not undergo gelation even at higher polymer content. As a result, the metal content of 10% was selected to be combined with hydrogen bonding interactions to synthesize multi-functionalized crosslinked system which would result in multi-responsive materials, as will be discussed in Chapter nine.

8.6 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 catalyst was purified by filtration using purified benzene under an atmosphere of argon. Spacer monomer **1**[7], SCS Pd pincer monomer **2**[8], were synthesized according to published procedures as described in Chapter three.

Characterization procedure

As reported in chapter three.

Polymerizations

The synthesis of the polymer **Poly-12** is described as a representative example: Monomers **1** (1.890 g, 7.56 mmol), **2** (646.86 mg, 0.84 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 55 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 after 6 hours, a drop of ethyl vinyl ether was added to terminate the polymerization, followed by prolonged drying at room temperature under high vacuum for 24 hours to remove all the solvent.

Crosslinking experiments

For all crosslinking experiments, the polymers were dissolved in a calculated amount of 1-chloronaphthalene and the mixture was stirred overnight at room temperature to ensure a homogenous solution. Then, a calculated amount of the crosslinking agent and silver tetrafluoroborate were added and the mixture was stirred, increase in the solution viscosity could be observed visually. The mixture was then allowed to anneal at $80^{0}C$ for a period of six hours, after which the sample was allowed to rest at room temperature for twelve hours before the rheological experiments were carried out.

The preparation of **Poly-12-3** is described as a representative example: **Poly-12** (176 mg, 0.06 mmol based on SCS groups along the polymer backbone) was dissolved in 1.584 g of 1-chloronaphthalene (10 weight %). Then 5.4 mg (0.03 mmol based on the metal coordination sites allowing for quantitative crosslinking) of **3** and 11.6 mg (0.06 mmol) of silver tertrafluoroborate were added to the sample and stirred. The mixture was then allowed to anneal at $80^{0}C$ for a period of six hours, after which the sample was allowed to rest at room temperature for twelve hours before the rheological experiments were carried out.

Rheological characterization

The rheological testing protocol of all polymer solutions has been described in Chapter five.

8.7 References

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CHAPTER NINE

MULTI-FUNCTIONAL CROSSLINKED POLYMER NETWORKS BASED ON HYDROGEN BONDING AND METAL COORDINATION

9.1 Abstract

Multi-functional reversible polymer networks based on hydrogen bonding and metal coordination have been synthesized by using a combination of ROMP and molecular self-assembly and characterized in detail with rheometry. The polymer scaffold consisted of a random poly(norbornene) functionalized with (i) cyanuric acid functional groups as hydrogen bonding moieties and, (ii) palladated SCS pincer centers as metal coordination sites. The hydrogen bonding interactions used for inter-chain crosslinking were based on three point cyanuric acid-2,4-diaminotriazine interactions. The hydrogen bonded networks exhibited thermo-reversibility. The metal coordination interactions for crosslinking were based on pyridine-Pd SCS complex. In both cases the extent of crosslinking could be controlled by varying the amount of the crosslinking agent added. By varying the noncovalent interaction used for crosslinking, materials with different rheological properties and responsiveness were obtained from the same parent polymer backbone.

9.2 Introduction

In chapter two it was explained how molecular recognition has offered a successful strategy to overcome certain limitations of covalently crosslinked polymer networks, such as polymer degradation, detrimental side-reactions during the curing process and, most importantly, the irreversible nature of covalent crosslinking. Molecular recognition processes based on noncovalent interactions (e.g. hydrogen bonding,[1,2] metal coordination,[3-5] Coulombic interactions[6,7]) have the advantage of being reversible and have thus enabled the development of crosslinked networks with tailored responsiveness towards a variety of external stimuli including temperature, solvent, and pH.[8] Examples include the use of metal coordination to obtain materials that are responsive to redox reactions and metal-ligand displacement agents[9,10], or the employment of hydrogen bonding interactions to create crosslinked polymer networks that are reveresible to temperature, as discussed in Chapters 5 to 7. However the present use of a single molecular recognition process in such networks limits the responsiveness to one external stimulus. By synthesizing polymers with multi-functional side-chains, it is possible to create noncovalent networks with unprecedented multi-responsiveness. In order to realize such networks, it is critical to use an orthogonal crosslinking strategy, i.e. the different noncovalent interactions should be mutually independent and non-interfering. The Weck group has synthesized highly functionalized noncovalently crosslinked polymers prepared from a single "Universal Polymer Backbone" via directional self-assembly processes using a combination of metal coordination and hydrogen bonding as was shown in Chapter two.[10]

In this chapter, a multi-functional crosslinking strategy will be discussed that uses terpolymers that combine crosslinking via hydrogen bonding interactions and metal coordination. It will be shown that the mechanical properties of such networks can be fine-tuned by choosing the appropriate noncovalent crosslinking agents. The extent of crosslinking can be manipulated by varying the amount of the crosslinking agent added. As a result, these materials offer a high degree of control on the final material properties and ultimately the underlying strategy shall be useful in designing tailor-made materials. Furthermore by utilizing a particular noncovalent interaction for polymer crosslinking, the responsiveness of the material can be tuned, for example hydrogen bonded crosslinked networks would be thermally responsive whereas utilizing metal coordination crosslinking would result in materials which could exhibit chemical responsiveness.

9.3 Research design

The research design is centered on two noncovalent interactions: hydrogen bonding and metal coordination. The hydrogen bonded complexes used in this chapter were described in Chapter 5 and are based on the cyanuric acid recognition motif, which is capable of multiple hydrogen bond formation by three-point hydrogen bonding between cyanuric acid and 2,4-diaminotriazine (Figure 9.1A). The metal coordination interactions, which were introduced in Chapter 8 are based of the coordination of pyridine to the SCS Pd centre (Figure 9.1B).

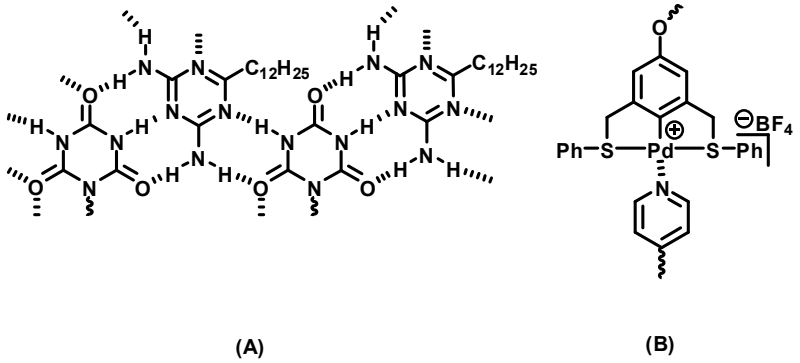


Figure 9.1 Self-assembly motifs employed: (A) Hydrogen bonded multi-point array based on three point hydrogen bonded complex between 2,6-diaminotriazine and cyanuric acid (B) Metal coordination interaction pyridine- SCS Pd metal coordinated complex.

The cyanuric acid and SCS Pd pincer complex moieties are anchored covalently onto a poly(norbornene) backbone by copolymerizing monomer **1** and the cyanuric acid containing monomer **2** using ROMP. As explained previously, the non-functionalized monomer **1** serves as a diluent for the cyanuric acid units and to increase solubility of all copolymers in non-polar solvent.[10] Hydrogen bonded crosslinking was carried by employing monotopic diaminotriazine-based crosslinking agent **4**, whereas the metal coordinated crosslinking was carried by the addition of crosslinking agent **5** after activation of the SCS Pd centers with silver tetrafluoroborate. All crosslinking events and experimental characterizations of the resulting polymer networks were carried out in 1-chloronaphthalene, which is a non-competitive, high boiling solvent in which all copolymers have good solubility. All monomers and crosslinking agents are shown in Figure 9.2.

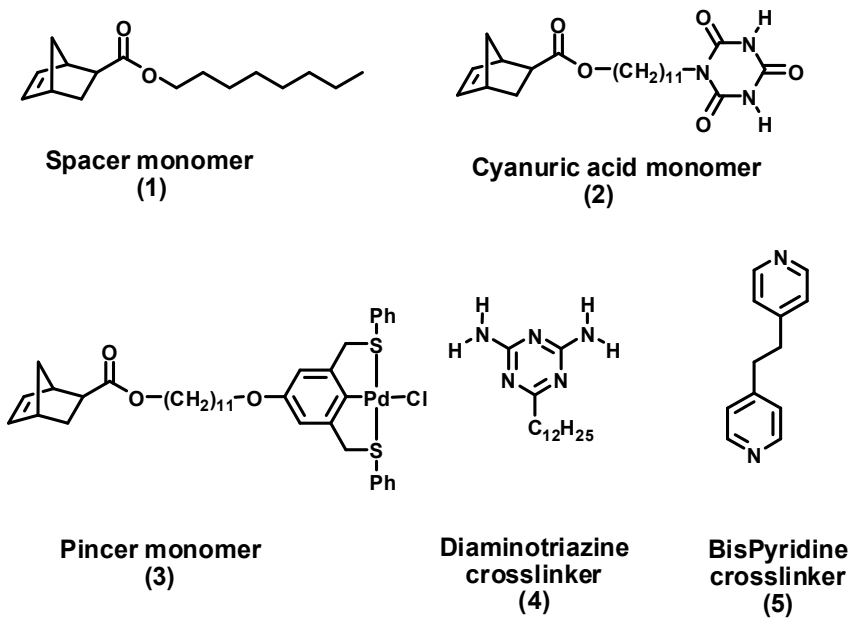
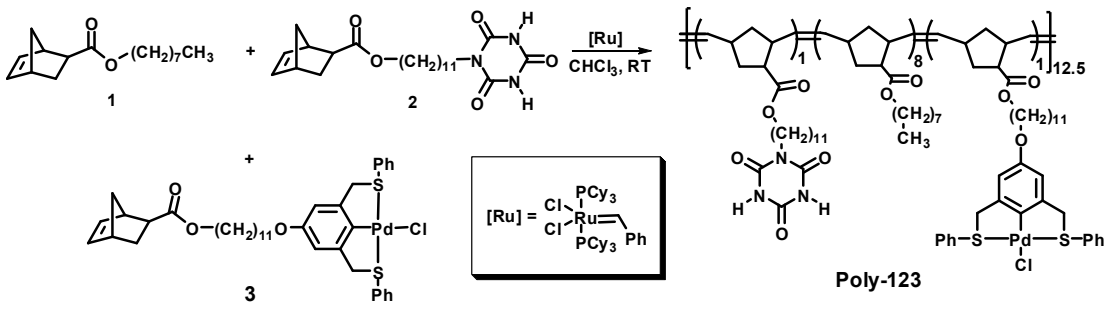


Figure 9.2 Monomers **1-3**, crosslinking agents **4** and **5** utilized in this study.

9.4 Results and Discussions

Copolymerization Studies

The polymerization behaviors of monomer **1-3** has been previously reported in detail.[11,10] All monomers can be copolymerized in a statistical manner via ROMP in chloroform at room temperature using Grubbs' first generation initiator (Scheme 9.1); complete monomer conversion was obtained within three hours at room temperature.



Scheme 9.1 Synthesis of **Poly-123** via ROMP using Grubbs' first generation initiator.

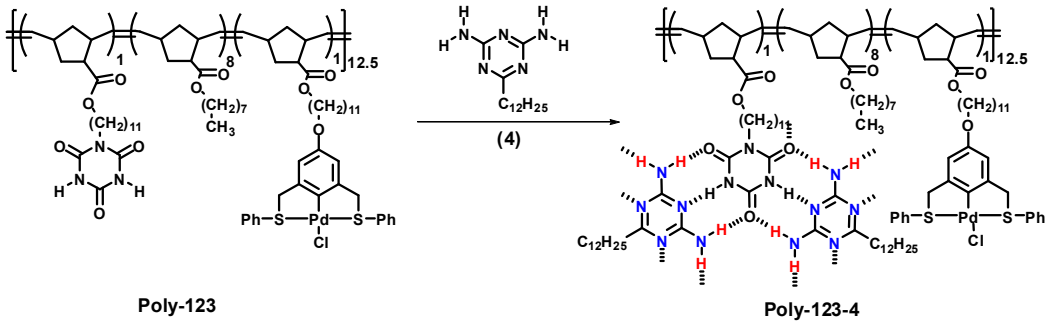
Copolymer composition and molecular weight are important parameters affecting the subsequent syntheses of homogenous crosslinked polymer networks in 1-chloronaphthalene, the solvent of choice for all our rheological measurements because of its relatively high boiling point. The solubility of all copolymers in 1-chloronaphthalene was dependent upon the mole fraction of **2**, as was demonstrated in chapter five. The copolymer composition for our rheological measurements was chosen to be 10 mol% of **2**. In chapter eightit was found that the optimum SCS pincer loading on the polymer is 10 mol% for a 10 wt% polymer concentration in solution. In line with these findings, the content of both **2** and **3** was kept at 10 mol% with a [M]/[I] = 125, resulting in terpolymers that were completely soluble in 1-chloronapthalene at room temperature. The weight average molecular weight was approximately 36000 and number average molecular weight was approximately 29 000 (M_w = 36 000, M_n = 29 000, PDI = 1.24).

9.5 Crosslinking studies

Terpolymer **Poly-123** can be seen as a multi-functional polymer scaffold which has crosslinkable side chains both for hydrogen bonding and metal coordination interactions. This multi-functional scaffold can be reversibly crosslinked in three distinct ways, i) via hydrogen bonding interactions through the addition of crosslinking agent **4**, which causes inter-chain crosslinking through the cyanuric acid groups, ii) via metal coordination interactions by the addition of crosslinking agent **5,** which causes inter-chain crosslinking through the activated SCS pincer Pd centers, ii) simultaneous crosslinking via both hydrogen bonding and metal coordination interactions.

9.5.1 *Hydrogen bonding crosslinking*

First, **Poly-123** was crosslinked through hydrogen bonding, using crosslinking agent **4** (Scheme 9.2).



Scheme 9.2 Noncovalent crosslinking of **Poly-123**, formation of hydrogen bonded network **Poly-123-4** via the addition of crosslinking agent **4**.

The degree of crosslinking could be controlled via the amount of crosslinking agent added. The concentration of **4** was varied from 0% to 100% (molar ratio of functional groups in the crosslinking agent to cyanuric acid groups attached to the polymer chains). The crosslinked networks were characterized quantitatively with rheology, but initial visual observations of the samples provided a telling qualitative picture of the mechanical properties. While solutions of **Poly-123-4** yielded a low-viscosity fluid below 20 mol % of **4**, higher concentrations of crosslinking agent **4** (above 25 mol %) resulted in the formation of an elastic solid that would not flow under gravity after vial inversion.

The crosslinking profile of **Poly-123** with **4** as the crosslinking agent is shown in Figure 9.3.

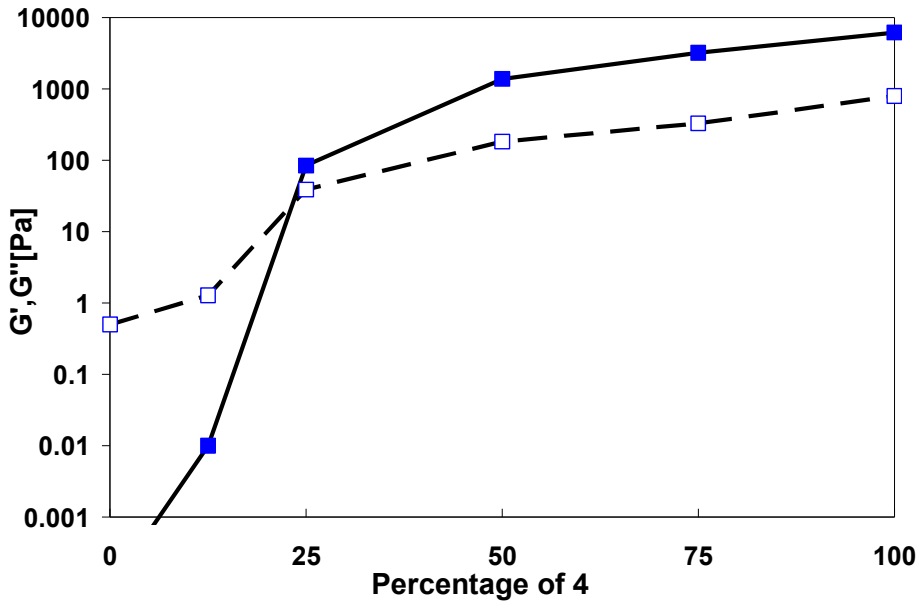


Figure 9.3 Crosslinking profile of **Poly-123** using **4**. Filled symbols denote the elastic modulus [*G′*], whereas empty symbols denote the loss modulus [*G″*] at strain value of 0.1 and angular frequency 6.28 rad/s. The concentration of **4** is defined relative to the molar concentration of cyanuric acid groups in the polymer solution.

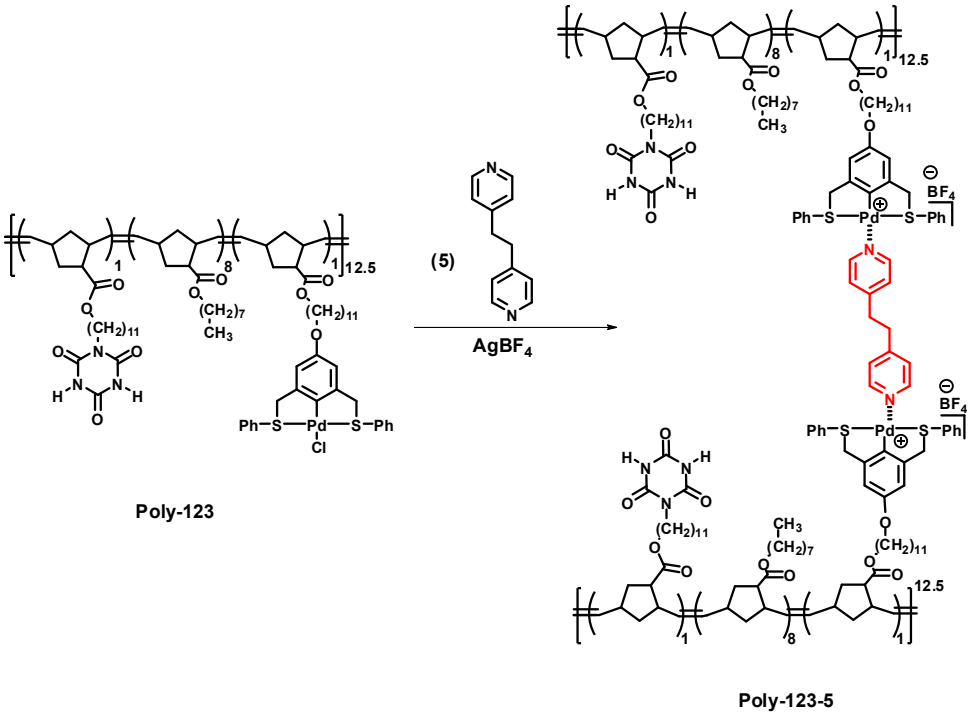
From the crosslinking profile it can be seen that the transition from viscous liquid to viscoelastic gel state takes place at low concentration of crosslinking agent **4**; even at 25 mol% of **4** the network exhibits a higher elastic modulus than loss modulus, indicating that **4** acts as a very efficient crosslinking agent, in line with the previous results in Chapter seven. The left vial in Figure 9.3 illustrates **Poly-123-4** at a 100% crosslinked composition.

(A) **(B)** **(C)**

Figure 9.4 Optical micrographs of inverted vials with (left) stable elastic gel (A) **Poly-123-4**, (center) (B) **Poly-123-5** and (right) (C) Poly**-123-45** at room temperature. All polymers and additives were dissolved in 1-chloronaphthalene. All the samples are at 100% crosslinked composition. Micrographs were taken two hours after inversion.

9.5.2 *Metal coordinated crosslinking*

The crosslinking of **Poly-123** via metal coordination occurs in two distinct steps: first the activation of the Pd centers by the abstraction of the chlorine atom through the addition of $AgBF_4$, followed by the coordination of the open Pd center by pyridine as shown in Scheme 9.3.[12,10,13] The 10 % (wt) solutions of **Poly-123** in 1-chloropnaphthalene were crosslinked by the addition of $AgBF_4$ or NH_4BF_4 and crosslinking agent **5**. To ensure homogeneity, the gels were allowed to anneal at 80°C for 4-5 hours before resting for at least twelve hours at room temperature before rheological analysis.



Scheme 9.3 Noncovalent crosslinking of **Poly-123**, formation of metal coordinated network **Poly-123-5** via the addition of crosslinking agent **5**.

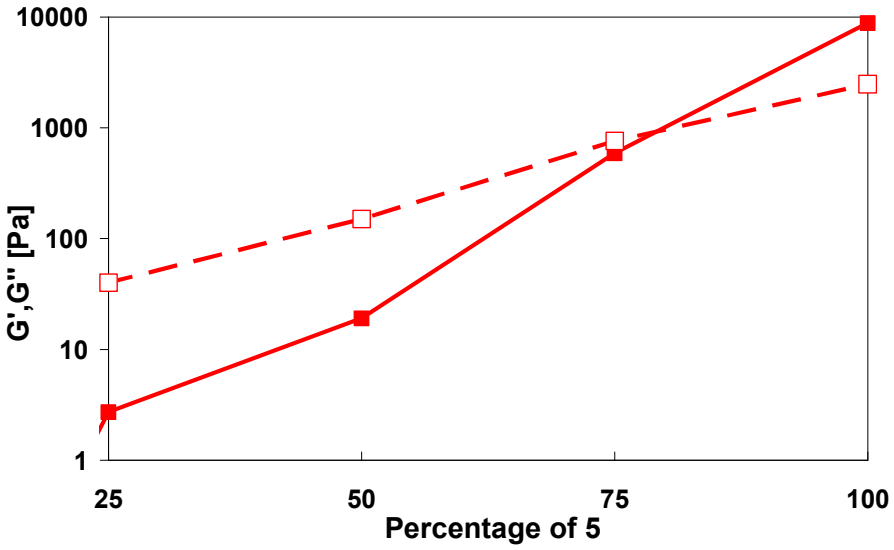
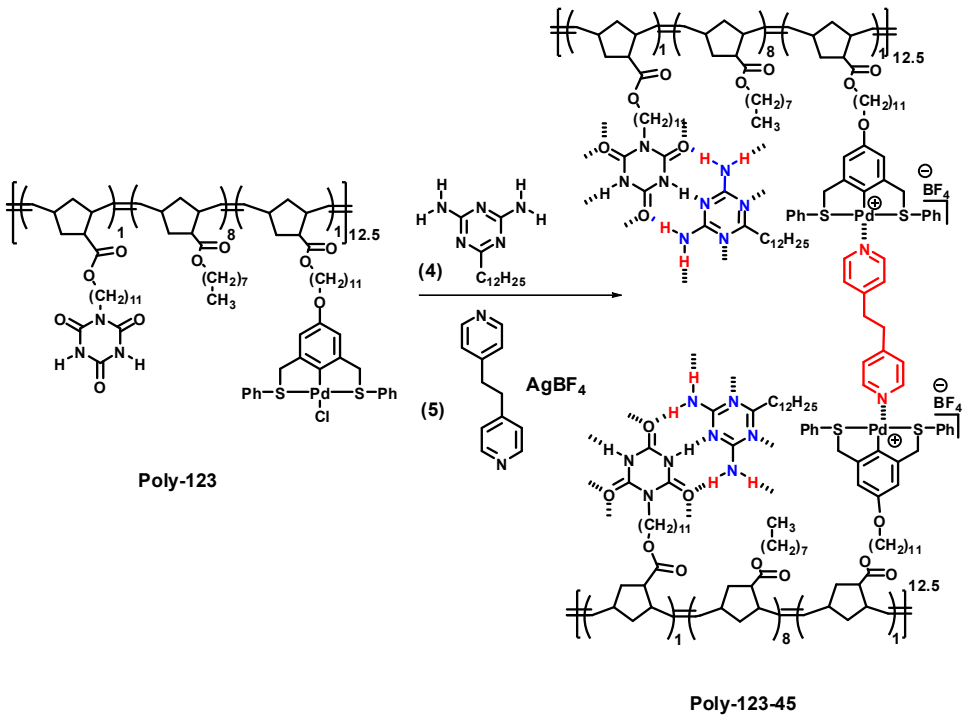


Figure 9.5 Crosslinking profile of **Poly-123** using **5**. Filled symbols denote the elastic modulus [*G′*], whereas empty symbols denote the loss modulus [*G″*] at strain value of 0.1 and angular frequency 6.28 rad/s. The percentage of **5** is based on the SCS palladium pincer complex groups attached to the polymer.

The degree of crosslinking was controlled by varying the concentration of **5** from 0 % to 100 % (molar ratio of functional groups in the crosslinking agent to pincer groups attached to the polymer chains). From the crosslinking profile it can be seen that the transition from the liquid to the viscoelastic gel state takes place at much higher concentration of **5** than for the hydrogen bonding agent. The network exhibits a higher elastic modulus than loss modulus only when the concentration of **5** is more than 80 mol%. Based on the the crosslinking profiles of Figures 9.3 and 9.5, it appears that **4** is a more efficient crosslinking agent than **5**. This can be attributed to the fact that hydrogen bonded network structure represents a true multi-point array network structure which has very high inter-chain connectivity due to the multi-hydrogen bonding interactions between the monotopic DAT and the cyanuric acid groups. On the other hand, the metal crosslinked network consists of very strong point-to-point linkages between the Pd centers and the pyridine units, but there is no multi-point array formation. As a result, a larger amount of crosslinking agent is required for the formation of the viscoelastic gel. The center vial in Figure 9.4 shows this experiment for a 100% crosslinking agent concentration.

9.5.3 *Simultaneous multi-functional crosslinking*

The orthogonality of hydrogen bonding and metal coordination interactions has been extensively discussed in the previous chapters[12,13] and enables simultaneous use of both interactions in the same system. Furthermore, the metal coordinated crosslinking step occurs at mild conditions and can be successfully combined with hydrogen bonding crosslinking as shown in Scheme 9.4.[12,10,13,14]



Scheme 9.4 Noncovalent crosslinking of **Poly-123,** formation hydrogen bonded as well as metal coordinated network **Poly-123-45** via the simultaneous addition of **4** and **5**.

The degree of crosslinking can be controlled by manipulating the concentration of both the crosslinking agents. Initially, the concentrations of both **4** and **5** were kept equimolar and were varied from 0% to 100% (molar ratio of functional groups in the crosslinking agent to cyanuric acid groups as well as the pincer groups attached to the polymer chains).

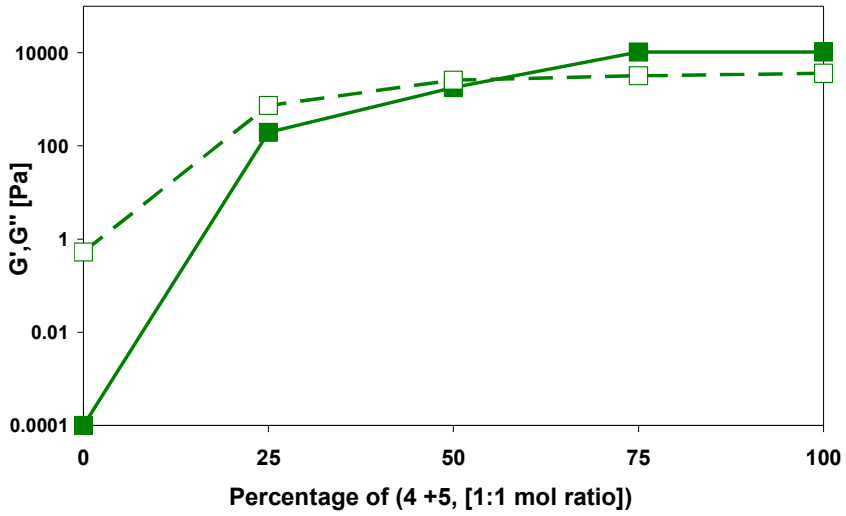


Figure 9.6 Crosslinking profile of **Poly-123** using **4** and **5** [1:1 mol ratio]. Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''] at strain value of 0.1 and angular frequency 6.28 rad/s. The percentage of **4** is based on the cyanuric acid groups attached to the polymer whereas percentage of **5** is based on the SCS palladium pincer complex groups attached to the polymer.

The crosslinking profile of **Poly-123-45** is depicted in Figure 9.6. The system undergoes gelation at about 57% crosslinking agent concentration, whereas **Poly-123-4** had a gelation point at around 25% and **Poly-123-5** had a higher gelation point at about 80%. It is not surprising that the gelation point of the multi-functional system falls in between the gelation points of **Poly-123-4** and **Poly-123-5**, since both interactions were specifically chosen for their orthogonality. The crosslinking profile also reveals that the combined the network is stronger (i.e. higher dynamic moduli), than either **Poly-123-4** or **Poly-123-5** at the corresponding crosslinking agent composition. This indicates that these two noncovalent interactions act synergistically to crosslink the network. Furthermore, Figure 9.6 shows that the dynamic moduli reach a saturation point above 80% crosslinked composition; further addition of the crosslinking agents does not increase the moduli of the network. This can be attributed to the network saturation state in which the network is

sufficiently crosslinked and further addition of the crosslinking agent does not increase the connectivity of the network.

9.5.4 *Rheological characterization*

In order to probe the effect of both crosslinking agents on network structure in more quantitative detail, oscillatory measurements with a cone-and-plate rheometer were carried out. Strain amplitude sweeps of **Poly-123-4, Poly-123-5** and **Poly-123-45** are shown in Figure 9.7; in all samples, the polymer concentration is 10 weight % and crosslinking agent concentration 100 %. It can be seen clearly that for all the samples the elastic modulus G' is greater than the loss modulus G'' indicating the formation of a gel according to a much more stringent rheological criterion than the vial inversion test in Figure 9.4. Furthermore **Poly-123-4** was prone to fracture at lower strain values as compared with **Poly-123-5** and **Poly-123-45,** consistent with the fact that cyanuric acid-2,4-diaminotriazine system exhibits a multi-point array system as discussed in Chapters 5 to7.

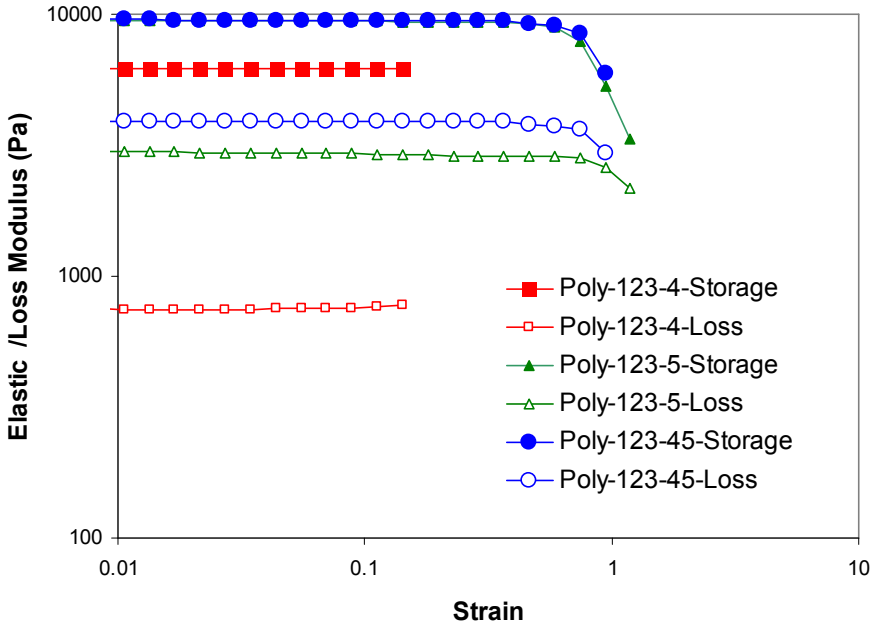


Figure 9.7 Strain amplitude sweep at 20°C at ω = 6.3 rad/s for **Poly-123-4** (squares), **Poly-123-5** (triangles) and **Poly-123-45** (circles). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''].

The viscoelastic behavior of these gels was further investigated by performing frequency sweeps at 20°C as shown in Figure 9.8. The figure clearly shows that the hydrogen bonded network has a much longer relaxation time, which falls well outside the frequency window of these experiments. On the other hand, the metal coordinated network show relaxation times between 0.1 and 1 rad/s.

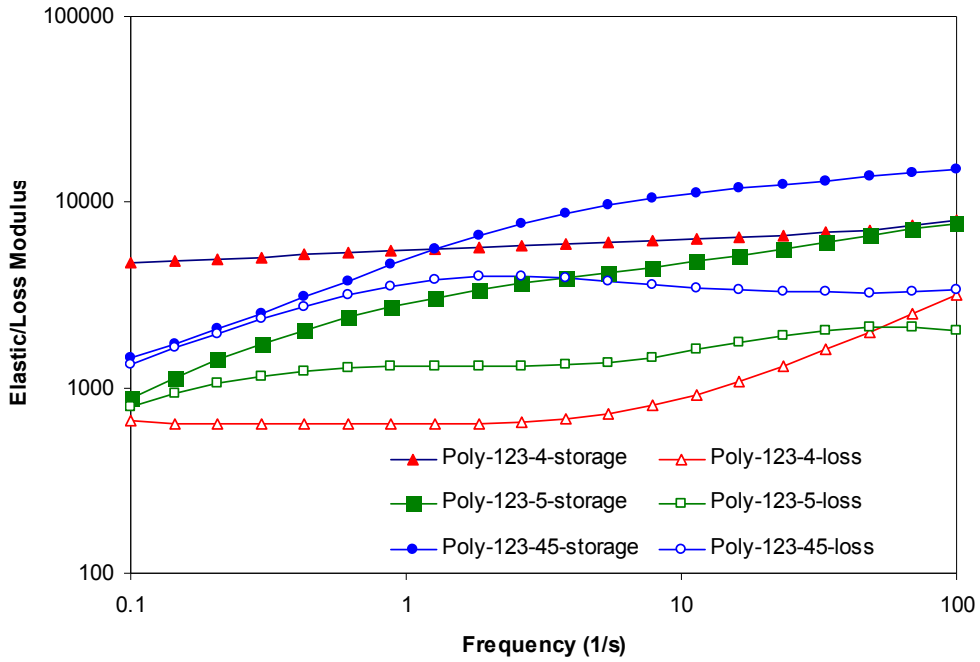


Figure 9.8 Frequency sweeps at 20°C at strain amplitude 0.1: (A) **Poly-123-4** (triangles), (B) **Poly-123-5** (rectangles), (C) **Poly-123-45** (circles). Filled symbols denote the elastic modulus [G'], whereas empty symbols denote the loss modulus [G''].

Hydrogen bonding is thermally reversible and in order to probe the responsiveness of the polymer networks, a temperature sweep was performed during which the sample was heated from 20 to 80°C, at a heating rate of 2°C /min, while monitoring the viscoelastic moduli at constant frequency (6.28 rad/s) and strain amplitude (0.1).

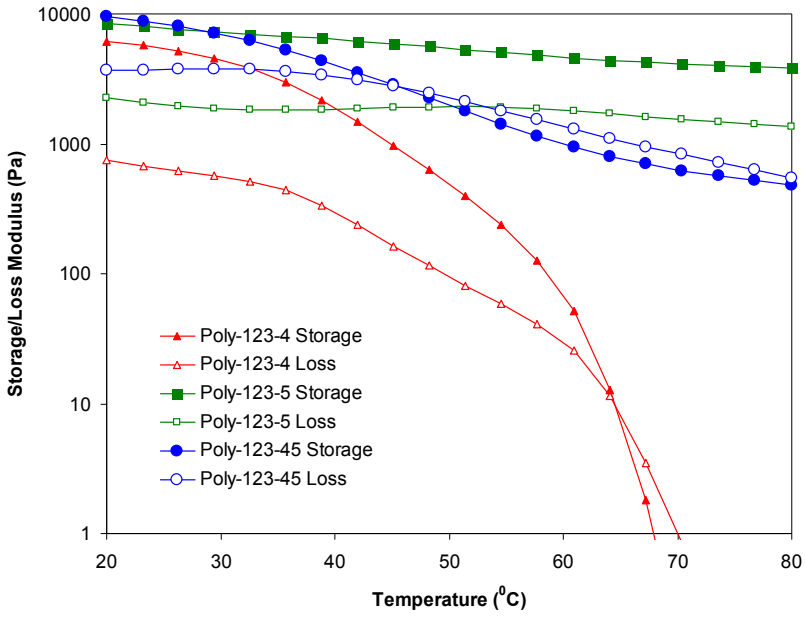


Figure 9.9 Temperature Sweep Profile from 80 to 20°C. *G'* and *G″* were measured at ω = 6.3 rad/s and strain 0.1: (A) **Poly-123-4** (triangles) (B) **Poly-123-5** (rectangles) and **(C) Poly-123-45** (circles).

The temperature sweeps in Figure 9.9 show a strong temperature dependence of the network based on **Poly-123-4** (Figure 9.9, triangles), which essentially becomes a low viscosity liquid at high temperatures. The decrease in moduli (by more than a factor ~10000) is much stronger than temperature related changes in viscosity for the pure solvent, which varies from 0.0028 Pa.s to 0.0013 Pa.s over the same temperature range. The decrease is attributed to the break-up of hydrogen bonded intermolecular associations. In contrast, the metal coordination crosslinking in **Poly-123-5** 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 9.9 (squares). Finally, the multi-functional crosslinked network **Poly-123-45** (Figure 9.9, circles) shows a clear thermal response, less than for the pure hydrogen bonded network but more than the metal crosslinked networks. However, the metal coordinated crosslinks are

sufficiently strong to to retain appreciable viscoelasticity even at high temperatures. By balancing the relative amounts of hydrogen bonding and metal coordinated crosslinking agents, the thermal response of the material can be controlled.

9.6 Summary and conclusions

In this chapter, random copolymers containing cyanuric acid groups and SCS palladated pincer complexes via ROMP have been synthesized. The resultant terpolymers were crosslinked either by hydrogen bonding, metal coordination or by a combination of both the interactions. The hydrogen bonding gels showed a greater thermal response than the metal crosslinked system, whereas the multi-functionalized system showed intermediate thermal response. Such a methodology in which different noncovalent interactions are utilized for inter-chain polymer crosslinking reactions can result in the creation of materials with diverse properties from the same parent polymer backbone.

9.7 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 purified benzene under an atmosphere of argon. Cyanuric acid monomer **2**,[11] spacer monomer **1**,[10] pincer monomer **3**, dodecyl-2,4 diaminotriazine **4** were synthesized according to previous reports.

Characterization procedure

As reported in chapter three.

Polymerizations

The synthesis of the terpolymer **Poly-123** is described as a representative example: Monomers **1** (3.6 g, 14.4 mmol), **2** (754.2mg, 1.8 mmol) and 3 (1.386 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 118.48 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 hours to remove all the solvent.

Poly-123 ^{1}H NMR (300 MHz CD_2Cl_2): 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): 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

Crosslinking experiments

Hydrogen bonded crosslinking

The preparation of **Poly-123-4** is described as a representative example: **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 weight %). Then 16.76 mg (0.06 mmol based on the hydrogen bonding sites allowing for quantitative crosslinking) of **4** was added to the sample and the suspension was heated until a clear homogenous solution was obtained, which quickly gelled when cooled to room

temperature. The gel was then allowed to rest at room temperature for least twelve hours before rheological measurements were carried out.

Metal coordinated crosslinking

The preparation of **Poly-123-5** is described as a representative example: **Poly-123** (190 mg, 0.06 mmol based on the metal coordination functional groups along the polymer backbone) was dissolved in 1.72 g of 1-chloronaphthalene (10 weight %). Then 5.5 mg (0.03 mmol based on the metal coordination sites allowing for quantitative crosslinking) of **5** and 11.68 mg of silver tetrafluoroborate were added to the sample and the mixture was stirred and annealed at 80 ^{0}C for at least six hours. The sample was then allowed to rest at room temperature for twelve hours before the rheological experiments were carried out. The samples gelled upon resting at room temperature after about 1-2 hours.

Multi-functional crosslinking

The preparation of **Poly-123-45** is described as a representative example: **Poly-123** (190 mg, 0.06 mmol based on the metal coordination functional groups along the polymer backbone) was dissolved in 1.72 g of 1-chloronaphthalene (10 weight %). Then 16.76 mg (0.06 mmol based on the hydrogen bonding sites allowing for quantitative crosslinking) of **4** with 5.5 mg (0.03 mmol based on the metal coordination sites allowing for quantitative crosslinking) of **5** and 11.68 mg of silver tetrafluoroborate were added to the sample and the mixture was stirred and annealed at 80 ^{0}C for at least six hours. The sample was then allowed to rest at room temperature for twelve hours before the rheological experiments were carried out.

Rheological characterization

The rheological testing protocol of all polymer samples has been described in Chapter five.

9.8 References

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(13) Pollino, J. M.; Stubbs, L. P.; Weck, M. "One-step multifunctionalization of random copolymers via self-assembly". Journal of the American Chemical Society 2004, 126, 563-567.

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Chapter TEN

Future Directions for Multi-Functionalized Side-Chain Functionalized Polymeric Systems

10.1 Introduction

As the field of functional materials design and synthesis continues to demand smaller and smaller size ranges for increasingly complex devices and applications, self-assembly has the potential to emerge as the most important tool available to scientists for the development of these materials. Supramolecular side-chain functionalized polymers combine the advantages of covalent polymer formation along with side-chain functionalization through noncovalent interactions.[1,2] As a result of the side-chain placement of the noncovalent complex, the main-chain of the polymer is independent of the stability of the noncovalent interaction, this allows for a vast number of polymer backbones to be used depending upon the desired application in mind. Such a system represents the synergistic combination of synthetic polymer chemistry with supramolecular chemistry and confers distinct advantages of using such strategy for materials design and optimization. Although the current development of synthetic polymer chemistry and supramolecular science shall greatly benefit the synthesis of more complex controlled polymer architectures using side-chain functionalization, multi-functionalized systems as of now are greatly under utilized. In this chapter the present scenario of multi-functionalized systems will be briefly discussed, focusing on the areas of improvement. Finally some potential applications of side-chain multi-functionalization will be discussed.

10.2 Present supramolecular multi-functionalized side-chain systems

The present examples of supramolecular side-chain copolymers reported in the literature are limited by two important factors. The first is the lack of multi-functionalization and second is the limited number of polymer scaffolds being used for side-chain functionalization.[1] Among the vast numbers of side-chain functionalized systems studied, only a handful of them use simultaneous noncovalent multi-functionalization limiting the applicability of these systems.[3-6] The second important limitation is the use of only a few of the large number of polymer scaffolds known for side-chain functionalization. Technologically as well as commercially important polymer scaffolds based on polyolefins, vinylics, poly(esters), poly(amides) etc have scarcely been used for multi-functionalization. These polymers scaffolds upon side-chain functionalization can give rise to novel materials which are based on commercially important materials and thus could offer more practical applications. One of the specific challenges of using the concept of side-chain multi-functionalization is the ability to functionalize commercially important polymer backbones to allow an extensive impact on the existing applications. Emerging functionally tolerant polymerization techniques such as ATRP, NMP, RAFT will allow for the synthesis of vast number of polymer backbones to be side-chain functionalized via copolymerization of the existing monomer with functionalized monomers.

10.3 Potential applications using multi-functional supramolecular side-chain functionalization

Three different potential applications of multi-functionalization in regards to existing systems in the literature will be discussed. The first will focus on the

employment of multiple hydrogen bonding interactions for tuning network properties. Multi-functionalization using hydrogen bonding and metal coordination will then be discussed in reference to blending of two incompatible commercial polymer backbones. The third potential application focuses on hybrid main-chain/side-chain systems involving hydrogen bonding and metal coordination interactions.

10.3.1 *Tuning the viscosity by using multiple hydrogen bonding interactions*

As seen in chapter seven, the use of multiple hydrogen bonding interactions allows one to tailor the micro-structure of networks, which in turn can be used to tailor the physical properties of materials. Such a system can be employed using commercially important polymer scaffolds such as poly(isoprene), poly(butadiene), poly(ethylene) etc which are normally above their glass transition temperatures at room temperature and can act as ideal commercial polymer backbones for room temperature-viscosity modulating systems. Chino and coworkers functionalized maleated poly(isoprene) with amino triazole to form a functionalized polymer with pendant triazole and carboxylic acid groups which resulted in self-dimerizing hydrogen bonded crosslinking. The inter-chain hydrogen bonded crosslinking enhanced the properties of the rubber[7]. The use of multiple complementary hydrogen interactions for polymer crosslinking will offer more advantages than using the self-dimerizing interactions used by Chino and coworkers.[8,9]

Figure 10.1 depicts the example of using poly(isoprene) as a commercial polymer backbone for such an application. Poly(isoprene) can be functionalized with cyanuric acid functional groups by copolymerizing cyanuric acid functionalized monomer with isoprene. Appropriate post-polymerization functionalization can also be used to get the functionalized poly(isoprene) backbone. The resultant functionalized polymer scaffold

can then be crosslinked by the addition of 2,4-diaminotriazine (or melamine) through complementary hydrogen bonding interactions (Path A, Figure 10.1) resulting in the formation of a viscoelastic multi-point array network. Since the inter-chain crosslinking involves complementary hydrogen bonding moieties, the physical properties of the material can be controlled by varying the degree of crosslinking by monitoring the amount of the crosslinking agent added to the system. Such modulation of the network properties is not possible in the self-dimerizing network employed by Chino and coworkers.

The physical properties of the network can be modulated by addition of the monotopic Hamilton Wedge (Path B, Figure 10.1), resulting in the disruption of the array network causing decrosslinking and lowering of the viscosity of the material. Furthermore, the extent to which the viscosity is lowered can be controlled by the monitoring the concentration of monotopic wedge agent added.

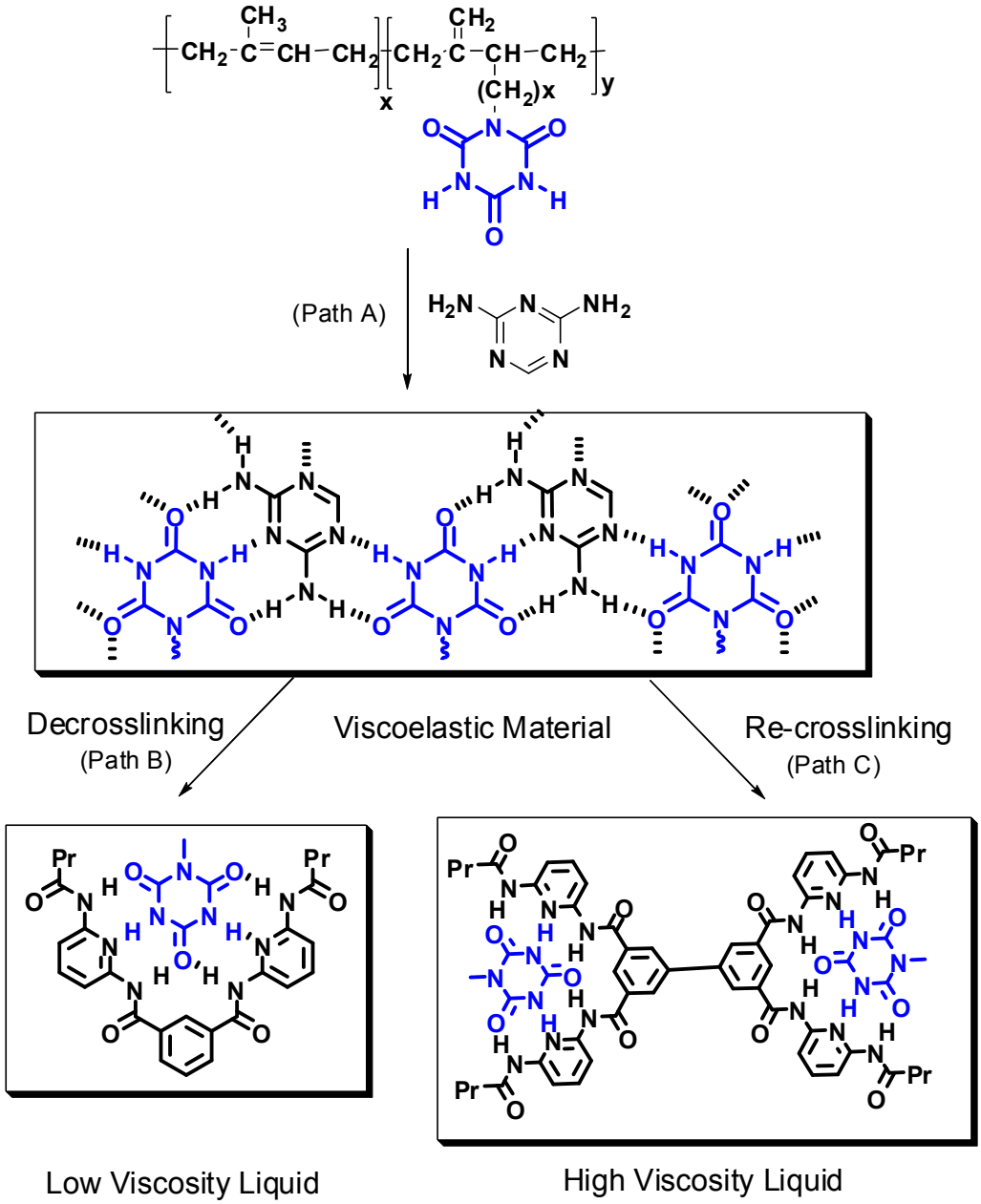


Figure 10.1 Modulating the physical properties of polyisoprene-based system by complementary multi-functional hydrogen bonding interactions.

Path C shown in Figure 10.1 depicts directed re-crosslinking of the cyanuric acids by the addition of a ditopic Hamilton wedge crosslinking agent which would result in the transformation of the viscoelastic gel to a highly viscous liquid. As explained in chapter

seven, the viscosity of the material can be tuned by monitoring the concentration of the ditopic crosslinking agent added.

Hence by using complementary multi-functionalized hydrogen bonding interactions, it is possible to optimize important materials properties such as viscosity reversibly and rapidly. Commercially important materials such as adhesives, coatings and elastomeric materials are potential targets for using this system.

10.3.2 *Polymer blends using multiple noncovalent interactions*

Noncovalent interactions especially hydrogen bonding and metal coordination offer new important strategies to blend two inherently incompatible polymers. Zimmerman and co-workers employed a four-point hydrogen bonding system between urea of guanosine (UG) and 2,7-diamido-1,8-naphthyridine (DAN) ($K_a \sim 5 \times 10^7\ M^{-1}$), to blend two immiscible polymers such as poly(styrene) and poly(butylacrylate).[10,11] This approach although offers advantages over conventional blend processes, the resultant hydrogen bonded blend is thermoreversible. As a result at higher temperatures due to the hydrogen bond disruption, the system has a high propensity for phase separation of the two polymer backbones. By combining metal coordination for polymer blending along with the hydrogen bonding interactions, the thermal response of the resultant blend can be fine tuned for a low thermal response with a high degree of metal crosslinking. Alternately one can increase the thermal response by using a high degree of hydrogen bonding crosslinking.

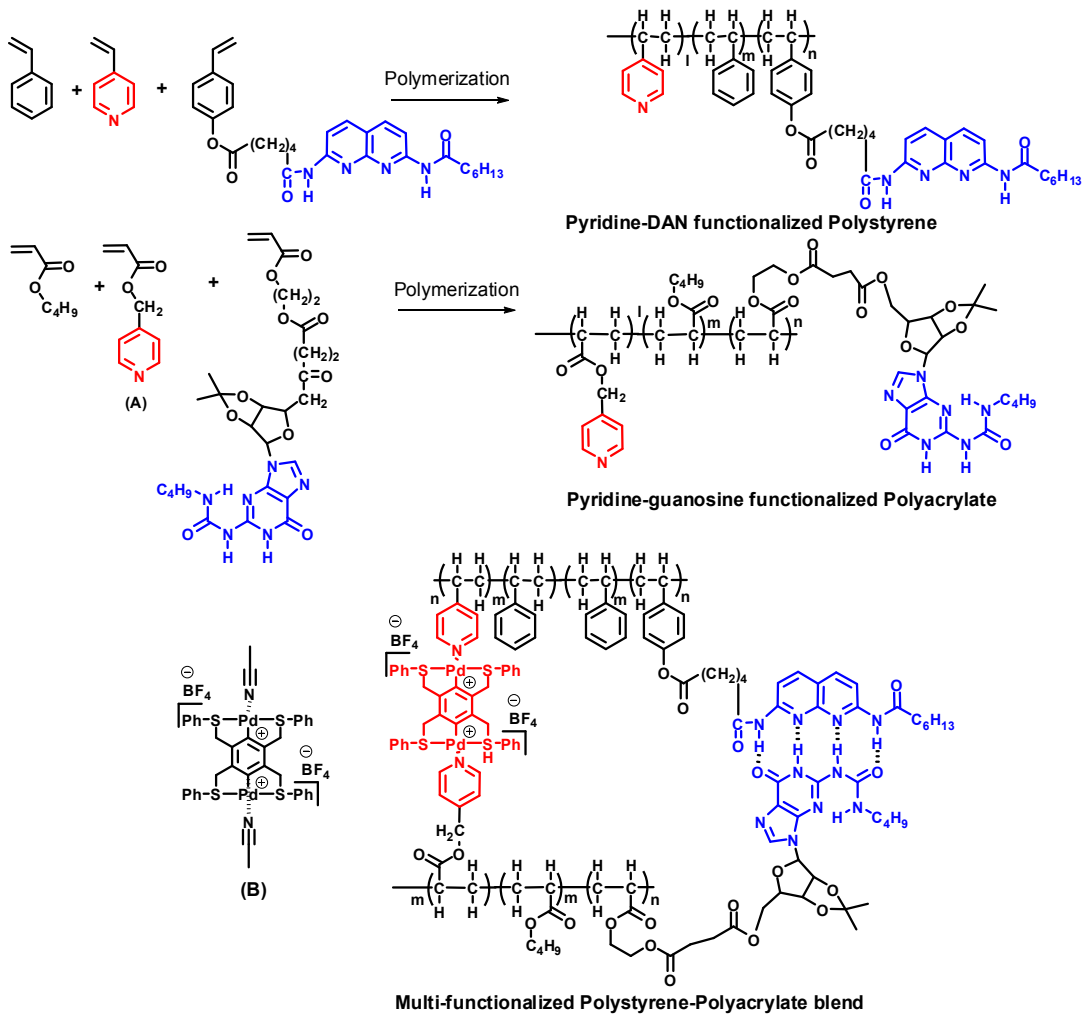


Figure 10.2 Multi-functionalized poly(styrene):poly(butylmethacrylate) blend using hydrogen bonding and metal coordination interactions.

Such a multi-functionalized polymer blend system using hydrogen bonding interactions based on the urea of guanosine (UG) and 2,7-diamido-1,8-naphthyridine (DAN) and metal coordination based on the SCS-Pd pincer-pyridine complex[12] is shown in Figure 10.2. In this system, both the polymers are side-chain functionalized with pyridine groups along with the hydrogen bonding functional groups, pyridine functionalized polymers have been crosslinked using ditopic SCS Pd pincer complex (**B**) before by Craig and coworkers.[13] Pyridine functionalized polymers can be achieved from

the existing system shown by Zimmerman. 4-Vinyl pyridine can be copolymerized with styrene, styrene-DAN monomers, to get the pyridine-DAN functionalized poly(styrene) backbone. Whereas by copolymerizing pyridine-functionalized acrylate monomer (**A**) with the butyl acrylate and the gaunosine functionalized monomer the pyridine-Guanosine functionalized polyacrylate polymer can be obtained.

The resultant multi-functionalized polystyrene and polyacrylate can be either blended via (i) hydrogen bonding between the DAN-Guanosine interactions to form a thermoresponsive blend, or (ii) metal coordination using a ditopic SCS Pd pincer crosslinking agent (B) to form a chemical responsive blend or (iii) simultaneous multi-functional crosslinking to obtain a multi-responsive blend which shows both chemical as well as thermal responsiveness.

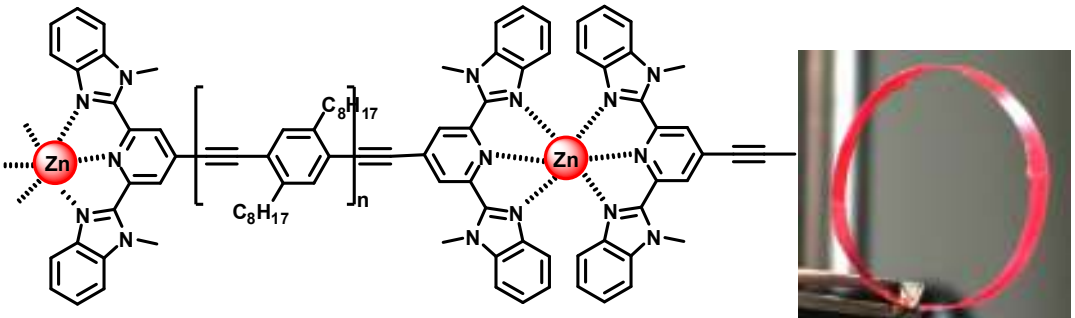
Hence side-chain multi-functionalization methodology for polymer blending can result in novel polymer blends whose properties can be tuned varying the functionalization technique used for the blending mechanism.

10.3 Multi-functionalized hybrid main-chain side-chain systems

Although the vast numbers of supramolecular main-chain as well as side-chain polymers have been reported in the literature, there are very few reports of main-chain/side-chain hybrid systems. These hybrid systems offer exciting possibilities of using multiple noncovalent interactions to form multi-responsive materials. Since the polymer backbone is composed of noncovalent complexes, it becomes imperative to use the stronger noncovalent complex to form the polymer backbone. The weaker noncovalent interaction can be used for side-chain functionalization or crosslinking reactions, which will not disrupt the polymer backbone.

Rowan and coworkers have utilized metal coordination interactions to form a main-chain supramolecular polymer with a conjugated polymer backbone.[14] They utilized Zn- methylbenzimidazolyl)pyridine (Mebip) complexes to form a supramolecular conjugated polymer based on poly(2,5-dialkoxy-p-phenylene ethynylene) core (Poly-A) as shown in Figure 10.3. By copolymerizing a cyanuric acid functionalized monomer, a multi-functional polymer scaffold will be obtained, which will consist of a main-chain supramolecular polymer consisting of metal coordination interactions with pendant cyanuric acid functional groups (Poly-B) as shown in Figure 10.3.

By using hydrogen bonding interactions the polymer can be either (i) reversibly functionalized using a monofunctionalized hydrogen bonded moiety[15] or (ii) reversibly crosslinked using a hydrogen bonding crosslinking agent[5] to form a thermoreversible polymer network which will also show chemical responsiveness due to the presence of the metal coordinated complexes in the main-chain.[16] Hence by using the appropriate noncovalent interactions for generating main-chain as well as side-chain hybrid systems, multi-stimuli responsive materials can be generated as desired.



(Poly-A)

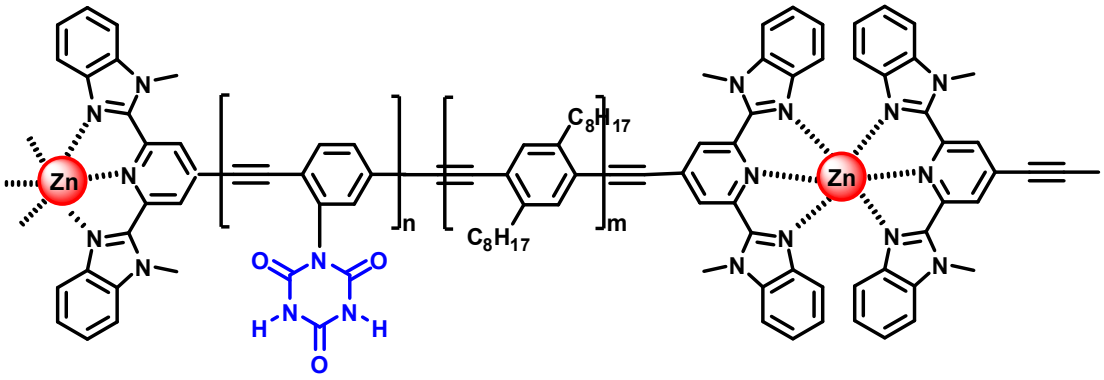


Figure 10.3 (PolyA)-Zn-PPE based metallo-supramolecular polymer, (Poly-B) - cyanuric acid side-chain functionalized (Poly-A). Inset: Photograph of a polymer film composed of Poly-A.[14]

10.4 Conclusions

This thesis began with the introduction of side-chain multi-functionalization concept as an alternative route to the highly complex and laborious covalent technique used conventionally for synthesizing highly functionalized polymers. The synthetic pathway to obtain such well-defined multi-functionalized polymers has been realized by the successful combination of ROMP and noncovalent chemistry. Furthermore, the orthogonality of these multiple interactions has also been established thus paving the way for their use in materials designing. To validate the practical applicability of this concept in the field of materials designing, the synthesized side-chain functionalized polymers were reversibly crosslinked using noncovalent interactions. It was seen that by using this concept, the mechanical properties of the networks could be controlled and modulated to a large degree. Furthermore, by using specific type of noncovalent interaction, it was also possible to tune the responsiveness of these materials towards external stimuli, thus making these materials potential candidates for "smart materials".

In conclusion, the work accomplished in the thesis has the potential to positively impact the field of supramolecular multi-functionalized side-chain copolymers. The multi-functionalization methodology has great potential for designing tailor-made materials and for understanding the structure-property relationship in supramolecular polymers. The ongoing advances in the field of supramolecular polymer chemistry will further open vast number of possibilities in the field of material designing, enabling easier synthesis, optimization and tuning of "smart materials" for emerging applications.

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