

Hydrogen Bonding Modules for Use in Supramolecular Polymers

Si Kyung Yang*^[a] and Steven C. Zimmerman*^[b]

Abstract: Supramolecular polymer chemistry has emerged as a major research focus within polymer science, because of the potential to improve material properties, through the combination of noncovalent interactions and synthetic polymers. As a supramolecular handle, the most useful noncovalent interaction is hydrogen bonding, which has been used extensively, because of advantages such as synthetic accessibility, directionality, fidelity, and, most importantly, re-

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sponsiveness to external stimuli. This review introduces recent advances in the development of hydrogen bonding modules that can be useful for creating a variety of supramolecular polymers. Furthermore, we present selected examples of hydrogen bonded supramolecular polymers from the literature, by dividing them into three categories: supramolecular polymers assembled from small molecules, and main-chain and side-chain supramolecular polymers.

1 Introduction

Nature utilizes a wide range of noncovalent interactions to maintain the well-defined, three-dimensional structure of key biomacromolecules, such as proteins, DNA, and RNA. Because their discrete structures are the key to their biomacromolecular function, noncovalent interactions truly underpin all biological complexity and function and, thus, life itself. Supramolecular polymer chemistry takes its inspiration from nature and has emerged as a major research focus in the past two decades.^[1,2] The incorporation of supramolecular interactions into polymeric systems can alter or improve the material properties of conventional polymers. Long before chemists began engineering these interactions into macromolecules, it was recognized that hydrogen bonding between polymer chains could have a profound effect on their properties. For example, the fact that Kevlar[®] has a tensile strength that is 7-fold higher than steel, on an equal weight basis, has been partly attributed to the formation of hydrogen bonds between amide NH and carbonyl groups.^[3] Likewise, the strength of Nylon 6,6 originates in the same type of sheet-like hydrogen bonding networks formed between polymer chains, whereas the elasticity derives from amorphous regions.^[4]

Given the remarkable properties provided by the noncovalent contacts in Kevlar[®] and Nylon 6,6, chemists saw a wide range of possibilities for new properties in supramolecular polymeric systems. For example, the loss of hydrogen bonding at higher temperature could lead to more easily processable polymeric materials, associated with relatively low melt viscosities. More generally, the over-

riding idea was that the reversible character of noncovalent interactions could lead to stimuli-responsive polymers, whose properties could be tuned by external stimuli, such as solvent, temperature, and light. In this context, a considerable effort has been focused on hydrogen bonding, because there is a lot known about how to tune its strength, and it is very responsive to environmental effects, especially solvent and pH.

There are two distinct and common ways to incorporate supramolecular motifs into polymers. When noncovalent interactions are employed to hold either monomeric or polymeric units together, main-chain supramolecular polymers are obtained.^[5] In contrast, noncovalent functionalization on the side-chains of covalent polymer backbones affords side-chain supramolecular polymers that may assemble into networks.^[6] In recent years, these two self-assembly approaches have been developed extensive-

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ly, in combination with the development of a variety of supramolecular motifs. The noncovalent interactions used in supramolecular polymer chemistry include hydrogen bonding, metal coordination, inclusion complexation, π - π stacking, and ionic and electrostatic interactions, with some overlap between these. The first two interactions are arguably the most commonly used supramolecular motifs. Indeed, metal coordination mediated supramolecular polymers have been reviewed recently.^[7] In this review, we focus on the development of hydrogen bonding modules over the past two decades and present some selected examples of hydrogen bonding-mediated supramolecular polymers, with an emphasis on our own research.

2 Hydrogen Bonding Modules

Due to inspiration from DNA base pairing, hydrogen bonding has been widely used in supramolecular polymer chemistry. Sometimes DNA and RNA nucleobases, themselves, are used, as they are commercially accessible, easy to link to other compounds, and provide high orthogonality (fidelity).^[8,9] However, the use of doubly hydrogen bonded complexes, such as the A·T base pair, can be limited by their relatively weak binding. Thus, a very large

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effort has also been invested in modifying the existing bases or developing entirely new heterocyclic subunits that pair analogously to DNA base pairs, but with additional hydrogen bonds that offer even higher stability and increased orthogonality.^[9-11]

A particularly useful feature of hydrogen bonding in the context of supramolecular polymer chemistry is its highly tunable strength and high responsiveness to a variety of external stimuli, such as solvent, pH, and temperature.^[12] The following sections provide a brief review of the development of hydrogen bonding modules, with a focus on the structural features that lead to their various levels of stability and orthogonality.

2.1 Triple Hydrogen Bonds

As indicated above, the concept of designing heterocycles to pair with different multiple hydrogen bonding motifs comes from nature, e.g., DNA, where two strands of nucleotides are held together by hydrogen bonding between their base pairs, which is responsible for stabilizing DNA's double helical structure.^[13]

Since the early 1990s, numerous efforts have been made to both develop and understand DNA base pair analogs, starting with Jorgensen's analysis of the effect of secondary electrostatic interactions between adjacent hydrogen bonds on the stability of triply hydrogen bonded complexes. It was proposed that AAD-DDA systems are significantly more stable than ADA-DAD analogs ($K_a \sim 10^4$ vs 10^2 M⁻¹), because of the additional stabilization achieved by attractive secondary interactions present in AAD-DDA arrays (Figure 1A).^[14]

In 1992, we reported that a complex with the AAA-DDD hydrogen bonding motif (Figure 1A), in which, unlike the two complexes above, only attractive secondary interactions are present, exhibits a very high association constant ($K_a > 10^5$ M⁻¹ in CDCl₃), consistent with Jorgensen's proposal.^[15] Subsequent investigations of related systems,^[16,17] as well as a more recent analysis of a large experimental dataset of base pairs and their analogs, were fully consistent with the proposal.^[18] These and other studies suggested an important design requirement for highly stable DNA base pair analogs: avoid alternating donor and acceptor groups. However, the dihydropyridine DDD receptor unit was chemically unstable. Later, the Anslyn group reported an *N*-protonated 2,6-diaminopyridine as a cationic DDD analog that overcomes the instability problem and enhances the hydrogen bond donating ability, thus forming more stable complexes with AAA species ($K_a > 5 \times 10^5$ M⁻¹ in CH₂Cl₂) (Figure 1A).^[19]

Recently, further investigations into the development of more robust AAA-DDD systems have been performed by Leigh and co-workers (Figure 1A).^[20] Their strategy was based on the extension of the AAA aromatic system used in the previous two complexes, i.e., 2,8-diphenyl-1,9,10-anthridine was replaced with a pentacene analog

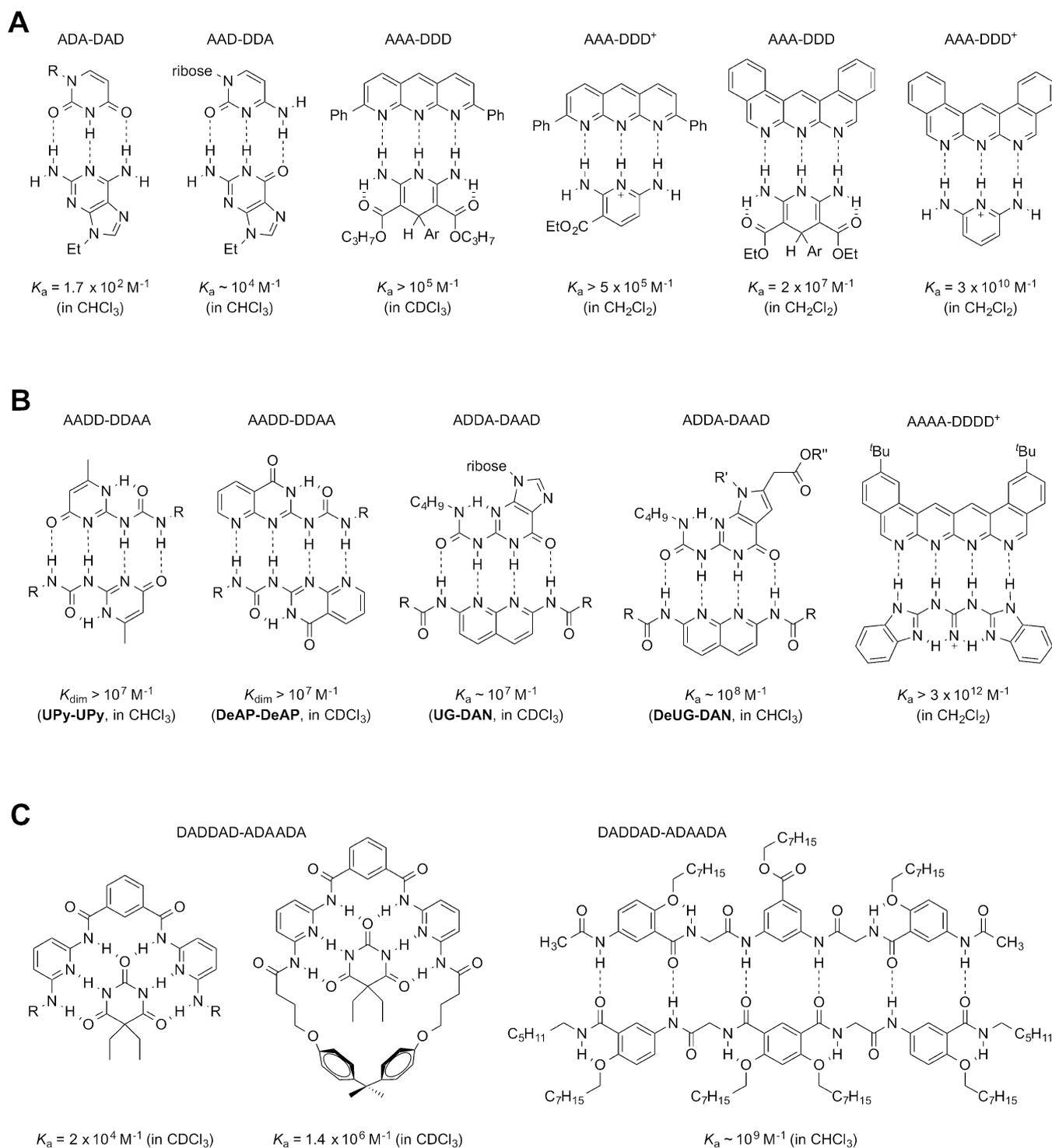


Figure 1. Hydrogen bonding pairs with multiple bonds. (A) Triple, (B) quadruple, and (C) sextuple hydrogen bonds.

that avoids the undesired hydride shift observed in the anhydridine based system and still binds to the dihydropyridine DDD receptor very strongly ($K_a = 2 \times 10^7 \text{ M}^{-1}$ in CH_2Cl_2). The stronger binding affinity can be attributed to an increase in the hydrogen bond accepting ability of

the pentacene-like AAA unit. They also found that such an acceptor unit is capable of forming the strongest known triply hydrogen bonded complex with Anslyn's cationic DDD unit ($K_a = 3 \times 10^{10} \text{ M}^{-1}$ in CH_2Cl_2), as determined by fluorescence spectroscopic titrations.^[21]

2.2 Quadruple Hydrogen Bonds

Quadruply hydrogen bonding units have also been developed to obtain complexes more stable than the triply hydrogen bonded pairs, and some of the examples are shown in Figure 1B. In 1997, the group of Meijer reported an outstanding self-complementary hydrogen bonding unit, ureidopyrimidinone (UPy), which has been used extensively by many other groups since then.^[22] The widespread use of UPy in supramolecular polymer chemistry comes from its one step synthesis and high dimerization constant ($K_{\text{dim}} = 6 \times 10^7 \text{ M}^{-1}$ in CHCl_3). The UPy dimer is very strongly held together by the four hydrogen bonds that arise from its AADD array of donor and acceptor groups. The UPy unit can also form a self-complementary ADAD tautomer, in which the enhanced repulsive secondary interactions weaken the dimer. We reported a similar hydrogen bonding unit in 1998, referred to as a deazapterin or DeAP unit.^[23] Like UPy, DeAP contains a self-complementary AADD array and strongly dimerizes ($K_{\text{dim}} = 9 \times 10^7 \text{ M}^{-1}$ in CHCl_3), irrespective of the tautomer present, and, indeed, was specifically designed to be the first DNA base analog where the presence of an alternative tautomer did not alter its fidelity of assembly.

Both self-complementary modules (UPy and DeAP) can also form highly stable ADDA-DAAD hydrogen bonded heterocomplexes with the diamido-naphthyridine (Napy/DAN) unit. However, their strong tendency to form dimers lowers the fidelity of the heterocomplexes and thus results in a lack of control over selective assembly processes. Therefore, use of these complexes in preparing complex macromolecular architectures, such as block copolymers, is limited. To avoid this problem, we sought to develop an alternative ADDA hydrogen bonding module with minimal dimerization constants. In 2005, we reported an interesting non-self-complementary unit, ureidoguanosine (UG), that is able to form a highly stable heterocomplex with DAN ($K_a \sim 10^7 \text{ M}^{-1}$ in CDCl_3), while exhibiting negligible self-association ($K_{\text{dim}} = 230 \text{ M}^{-1}$ in CDCl_3).^[10,24] We also demonstrated that such high stability and fidelity of the UG-DAN complex made it useful in assembling two chemically different polymeric blocks to produce supramolecular alternating multiblock copolymers.^[25] We pursued this particular unit by reporting its deaza analog (DeUG), initially designed to further increase the binding strength and fidelity. Although the DeUG displays a dimerization constant of $K_{\text{dim}} = 880 \text{ M}^{-1}$ higher than that of UG, the design allows for much stronger complexation with DAN ($K_a \sim 10^8 \text{ M}^{-1}$ in CHCl_3).^[26] Moreover, convenient synthetic methods to obtain DeUG on a multi-gram scale and to incorporate clickable functional handles on it have been recently reported.^[27]

As described in the previous section, the strongest triply hydrogen bonding pairs contain the AAA-DDD array, which possesses only attractive secondary interactions, unlike the other two arrays. Likewise, in the case of

quadruply hydrogen bonded complexes, an AAAA-DDDD array would be expected to have the maximal binding strength. The considerable synthetic challenge to prepare such units has recently been successfully met by Leigh and co-workers. Thus, they reported a cationic AAAA-DDDD complex that exhibits exceptional binding strength ($K_a > 10^{12} \text{ M}^{-1}$ in CH_2Cl_2).^[28] In particular, this complex was stable even in very polar solvent systems ($K_a \sim 10^6 \text{ M}^{-1}$ in CH_3CN and $K_a \sim 10^5 \text{ M}^{-1}$ in 10% DMSO/ CHCl_3), making it a promising candidate for supramolecular polymer applications.

2.3 Sextuple Hydrogen Bonds

Several sextuply hydrogen bonded complexes have been developed, and one of the most notable is that between diaminopyridine-substituted isophthalamide, often referred to as the Hamilton receptor, and either barbituric acid or cyanuric acid (Figure 1C).^[29] This non-self-complementary recognition pair is highly robust ($K_a = 2 \times 10^4 \text{ M}^{-1}$ in CDCl_3), and its macrocyclic derivative exhibits an approximately 100-fold increase in the association constant. The Hamilton receptor has been used extensively in supramolecular polymer chemistry, since the late 1980s. Together with the Upy dimer, these recognition systems have clearly obtained what might be referred to as privileged status.

Gong and co-workers reported a very stable sextuply hydrogen bonded duplex ($K_a \sim 10^9 \text{ M}^{-1}$ in CHCl_3), by extending their initial oligoamide-based linear arrays, in which intramolecular hydrogen bonding plays a key role in providing a preorganized, planar arrangement of the donor and acceptor groups (Figure 1C).^[30] In later work, Gong reported the ability to maintain the oligoamide-based duplexes in aqueous media by combining hydrogen bonding and dynamic covalent interactions.^[31] Building on the naphthyridine unit, Corbin and Zimmerman reported that hetero-complementary bis-ureidonaphthyridines and bis-naphthyridinoureas form sextuply hydrogen bonded duplexes, although the individual units can pair intramolecularly, which reduces the duplex stability.^[32]

3 Hydrogen Bonded Supramolecular Polymers

Supramolecular polymers can be defined as polymeric materials self-assembled via noncovalent interactions. There are many types of supramolecular polymers, classified by the type of repeating units (monomers and polymers), recognition motifs (hydrogen bonding, metal coordination, host-guest interactions, etc.), and self-assembly location (main-chain and side-chain). In this section, we focus solely on hydrogen bonded supramolecular polymers and present selected examples reported in the literature. In general, these polymers can be prepared in three different ways: (i) supramolecular polymerization of

small molecules, (ii) self-assembly of telechelic polymeric building blocks, and (iii) noncovalent functionalization of recognition units on the side-chains of a polymer.

3.1 Supramolecular Polymerization

In the first approach, monomers based on small molecules containing two sites with the potential to form noncovalent bonds are self-assembled into a polymer chain, in a process termed as supramolecular polymerization. This process is analogous to traditional polycondensation, but involves noncovalent linkages between the repeating units, instead of covalent bonds.^[1,2] In 1990, the group of Lehn first reported this type of supramolecular polymer, in which bifunctional diamidopyridines and bifunctional uracil derivatives self-assembled into linear polymeric chains, via triple hydrogen bonding interactions (Figure 2A).^[33] In contrast to the behavior of each pure monomer, the supramolecular polymers obtained through self-assembly of a 1:1 mixture of the two monomers displayed liquid crystalline phases, and the properties could be tuned by altering the rigidity of the spacers within the bifunctional recognition units.

In addition, quadruply hydrogen bonding units have been employed for supramolecular polymerization. In seminal work, Meijer and co-workers reported that bifunctional small molecules containing two self-complementary UPy units are capable of forming linear supramolecular polymers with molecular weights that can be tuned by varying the solvent, concentration, and purity of the monomers (Figure 2B).^[22] Most significantly, the supramolecular polymer exhibited physical properties analogous to covalent polymers. It was important that the UPy-based monomers be highly purified for formation, in

chloroform, of a polymer with a high degree of supramolecular polymerization. Thus, mono-functional UPy impurities acted as chain-termination agents, thereby lowering the degree of polymerization.

3.2 Main-Chain Supramolecular Polymers

Main-chain supramolecular polymers can be defined as polymers that are held together by noncovalent interactions along their main-chain. There are many architectures possible, ranging from polymers with a single end-group that dimerize to divalent monomers or telechelic polymers with recognition units at both ends, which allow multiple subunits to assemble linearly (see below). When the self-assembly involves monomers or macromonomers with different structures, it is possible to form supramolecular block copolymers.

Combining the phase separation behavior of block copolymers with the responsiveness of supramolecular materials can lead to some interesting properties. For example, the Hawker and Meijer groups reported a supramolecular AB diblock copolymer assembled via quadruply hydrogen bonding modules (Figure 3A).^[34] They synthesized poly(benzylmethacrylate) and poly(butyl acrylate) homopolymers, functionalized with UPy and Napy, respectively, at one chain-end. The UPy-Napy complexation resulted in the formation of supramolecular diblock copolymers. Gong and co-workers introduced their sextuply hydrogen bonding motifs in the chain-ends of poly(styrene) (PS) and poly(ethylene glycol) (PEG), to obtain two complementary homopolymers capable of self-assembling into an AB diblock copolymer (Figure 3B).^[35] A similar architecture was achieved by the Weck and co-workers,^[36] using the sextuple hydrogen

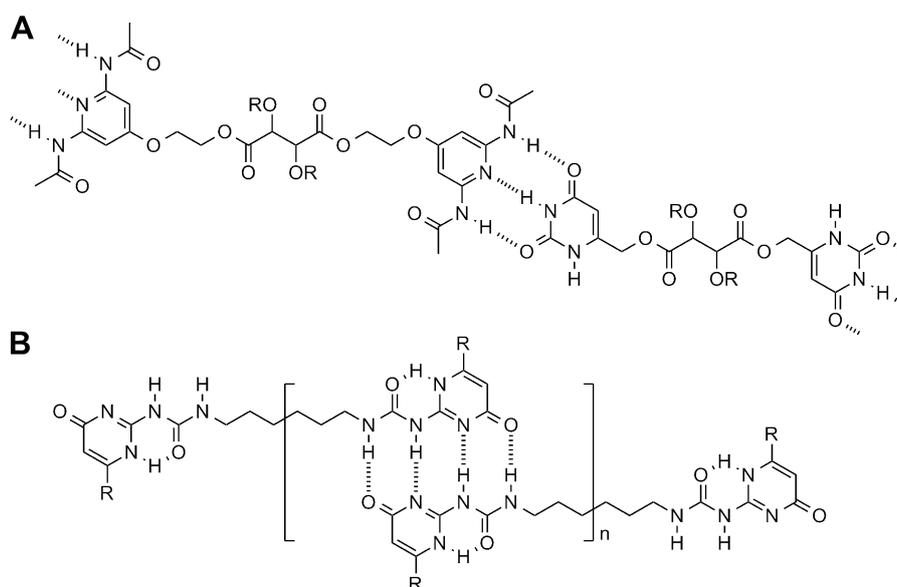


Figure 2. Supramolecular polymers self-assembled from small molecules.

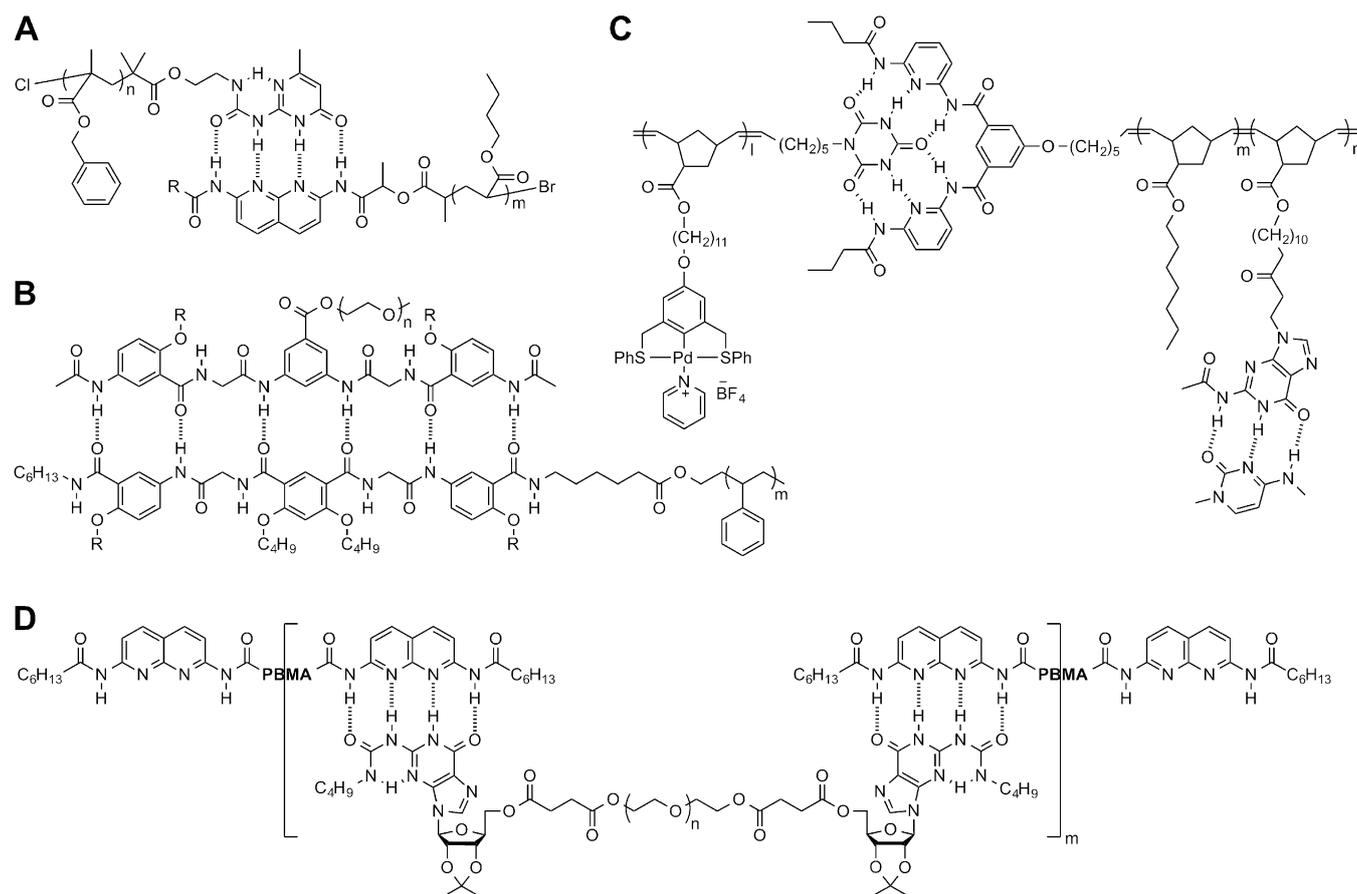


Figure 3. Examples of main-chain supramolecular polymers based on hydrogen bonding. PBMA = poly(butyl methacrylate).

bonding between the Hamilton receptor and cyanuric acid. In this example, the resulting supramolecular AB diblock copolymer consisted of two different poly(norbornene)s (PNBs) that contain additional noncovalent recognition units on their side-chains, allowing the creation of even more complicated supramolecular polymeric materials (Figure 3C). Weck and co-workers extended this general approach to the self-assembly of ABA and ABC triblock copolymers, which required the use of a central telechelic B block. The B block, with identical recognition end-groups, assembled with two A units to form the ABA architecture, whereas two orthogonal recognition end-groups bound A and C blocks, respectively, to afford the first supramolecular ABC triblock copolymer.^[36,37] In the latter approach, two orthogonal hydrogen bonding interactions, the Hamilton receptor-cyanuric acid and UG-DAN pairs, were employed to linearly connect the three different homopolymers via both stepwise and one-pot self-assembly.^[37]

Another class of main-chain supramolecular polymers is multiblock copolymers, which can be prepared by supramolecular polymerization of two different symmetrically end-functionalized polymers as the macromolecular

repeating units, different from the small molecule based system above. For example, Binder and co-workers utilized the triply and sextuply hydrogen bonding pairs, thymine-triazine and the Hamilton receptor-barbituric acid, respectively,^[38] to combine two strongly phase-separating polymers, poly(isobutylene)s and poly(etherketone)s, thereby affording pseudo multiblock copolymers with thermal behaviors which depend on the association strengths of the hydrogen bonding pairs employed. In addition, the Meijer and Sijbesma group was able to obtain supramolecular alternating block copolymers using quadruple hydrogen bonding interactions between DAN (Napy) and UPy.^[39] Similarly, we developed a supramolecular alternating block copolymer with a PEG block containing UG end-units and poly(butylmethacrylate) with DAN end-units (Figure 3D).^[25]

One of the interesting aspects of the alternating supramolecular block copolymers is how the self-assembled architecture is affected by the fidelity (orthogonality) of the recognition unit pairing.^[25] Because UPy is capable of strong dimerization, addition of extra bis-UPy units leads to elongation and formation of a UPy block within the alternating block copolymer. In contrast, our UG and DAN

units exhibit such high fidelity assembly that addition of the bis-UG or bis-DAN unit beyond the 1:1 mixture causes chain shortening, as the excess monomer acts as a chain stopper.

3.3 Side-Chain Supramolecular Polymers

Hydrogen bonding interactions have also been employed widely for the modification of side-chains along polymer backbones, producing highly functional polymeric materials with tunable properties. Since the early work on side-chain liquid crystalline polymers based on hydrogen bonding by Fréchet and Kato,^[40,41] the research focus on the hydrogen bonded side-chain supramolecular polymers has moved to recognition motifs that are closely related to natural hydrogen bonding pairs. For example, the thymine and diamidopyridine recognition pair utilizes three hydrogen bonds, allowing for strong binding affinity.

Rotello and co-workers have reported the hydrogen bonding mediated functionalization of polymers containing triazine or diamidopyridine on the side-chains.^[42,43] Using such a noncovalent side-chain functionalization strategy, named “plug and play,” they were able to synthesize a library of functional composite materials, by allowing various small molecules, including flavin and thymine derivatives, to self-assemble onto the polymers (Figure 4A).^[44] This strategy was further expanded to include applications in nanoscience, described as “brick and mortar” self-assembly.^[45] In this approach, the diamidopyridine-functionalized polymer (mortar) serves as glue between gold nanoparticles (bricks) containing complementary thymine receptors, thereby directing the self-assembly. In most cases, Rotello and co-workers used poly(styrene) copolymers that required post-polymerization reaction, because of the incompatibility of the recognition motifs with the free radical polymerization methods used to obtain the poly(styrene) backbones.

This problem can be overcome by using highly controlled, living, and functional group tolerant polymerization methods. In this manner, the groups of Rotello,^[46] Sleiman,^[47,48] and Weck^[49] have employed ring-opening metathesis polymerization (ROMP) to produce well-defined side-chain supramolecular polymers based on PNB backbones. For example, the Rotello group synthesized rigid ROMP polymers, bearing complementary diamidopyridine and uracil units, and investigated their self-assembly into spherical polymersomes that slowly fuse to form larger structures.^[46] The Sleiman group also employed ROMP, to obtain adenine-functionalized copolymers capable of folding into cylindrical morphologies, as a result of the self-complementary hydrogen bonding of the adenine units.^[47,48] The Weck group reported the effect of the hydrogen bonding moieties on the ROMP behavior of diamidopyridine- and diamidotriazine-functionalized norbornene monomers, as well as the self-as-

sembly of the resulting polymers with thymine-based molecules, to produce highly functionalized polymers.^[49]

We incorporated UG and DAN into the side-chains of two immiscible polymers, poly(butyl methacrylate) (PBMA) and PS, respectively (Figure 4B), with the goal of using the energy of hydrogen bonding to drive the formation of a polymer blend.^[50] Indeed, the UG-DAN heterocomplex, as a result of its high stability and fidelity, allowed for the formation of a homogeneous blend. Specifically, a mixture of UG-PBMA and DAN-PS resulted in colorless, transparent films, without phase separation. Interestingly, even 4 mol% of the recognition units in the polymers was sufficient to form the supramolecular network structure with tunable and thermoreversible properties.

Very recently, we used the DeUG and DAN units as nanoscale adhesion promoters of macroscopic adhesion.^[51] In this study, DAN units were incorporated into the side-chains of PS, via a C-H activation methodology, whereas glass surfaces were functionalized with complementary DeUG units in a more traditional way. Mechanical tests of the supramolecular adhesive system revealed that the quadruple hydrogen bonding employed plays a key role in the macroscopic adhesive properties. Two aspects of this study were most noteworthy. First, the supramolecular adhesive set at room temperature gave adhesive bonds that were comparable to the covalent adhesion of polystyrene-*co*-maleic anhydride heated at 150 °C between glass slides functionalized with (3-aminopropyl)triethoxysilane (APTES). Secondly, once the supramolecular adhesive bond fails, the bond between the glass plates can be reset with just a drop of solvent, and the reset system gives about 55% recovery of virgin shear strength.

Weck and co-workers have employed three different recognition units along polymer chains, namely the cyanuric acid unit, the palladated sulfur-carbon-sulfur (SCS) pincer ligand, and the thymine receptor units. These three recognition units orthogonally complex the Hamilton wedge (via sextuple hydrogen bonding), pyridine units, and diaminopyridine containing compounds and materials, respectively.^[52,53] All three were shown to function together, and subsets containing two motifs have also been examined. For example, in the latter case, random and block copolymers containing the two distinct hydrogen bonding modules, cyanuric acid and thymine, were synthesized via ROMP and then self-assembled with the complementary Hamilton receptor and diaminopyridine units, respectively (Figure 4C).^[54]

The orthogonal multi-functionalization of the copolymers was achieved simply by a one-step self-assembly process, described as self-sorting of polymers. The Weck group also prepared thermoreversible, cross-linked polymer networks, using two complementary hydrogen bonding interactions, specifically between cyanuric acid and the Hamilton receptor or diaminotriazine (Figure 4D).^[55]

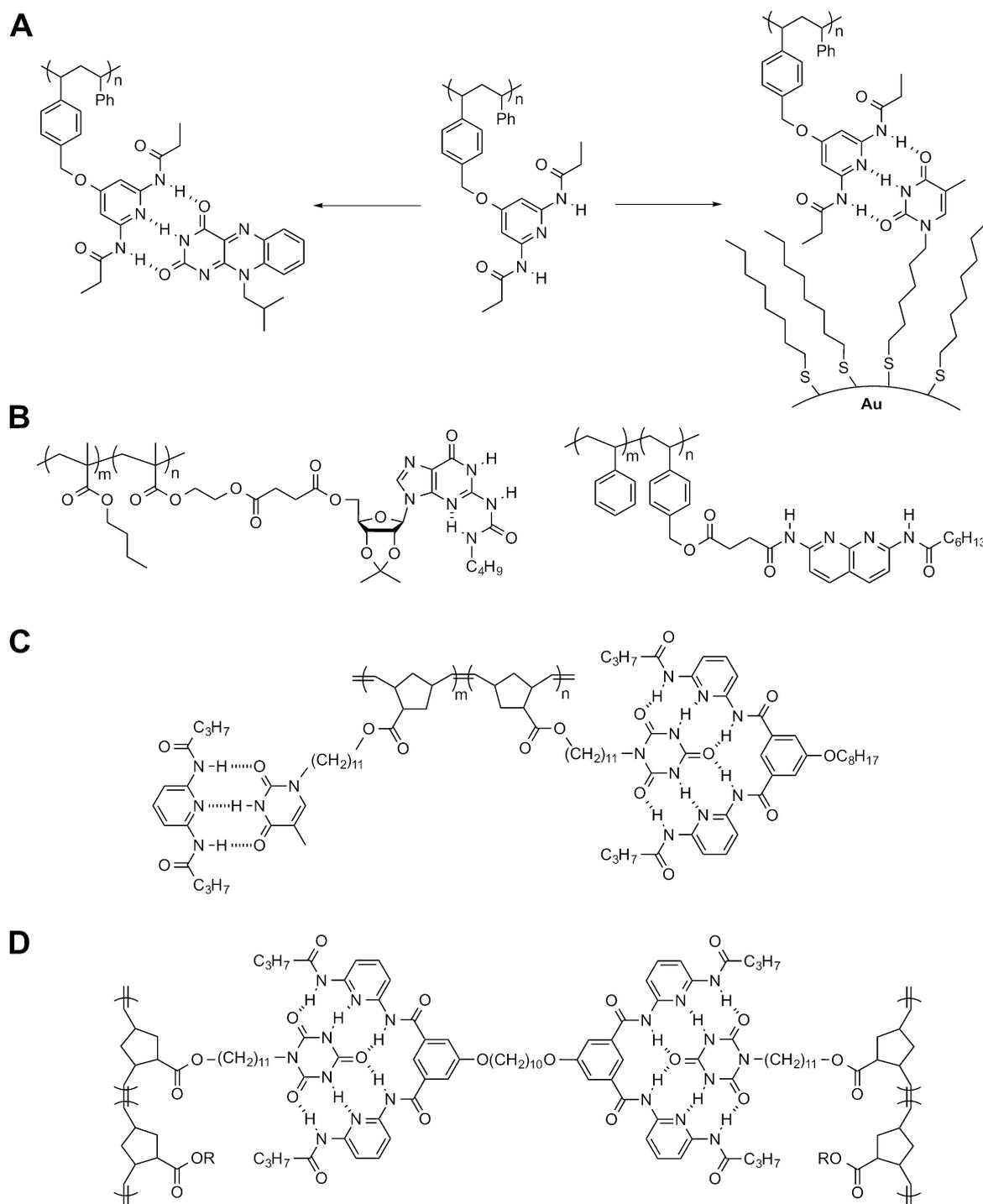


Figure 4. Examples of side-chain supramolecular polymers based on hydrogen bonding.

In this study, the polymer scaffold was functionalized with cyanuric acid units, and the addition of ditopic cross-linking agents, based on the complementary recognition units, resulted in inter-chain hydrogen bonding interactions. The degree of cross-linking and rheological properties could be controlled by varying the amount of the cross-linking agents added and the hydrogen bonding

motifs of the cross-linking agents, respectively. Recently, the same group reported that the mechanical properties of the polymeric networks could be modulated at room temperature by altering the hydrogen bonding interactions employed for the inter-chain cross-linking process.^[56]

4 Summary and Outlook

Inspired by nature's masterful use of noncovalent chemistry to create a wide variety of biological materials, as well as the recognition that the special properties of Kevlar® and Nylon 6,6 originate in hydrogen bonding, polymer chemists have started to incorporate designed noncovalent interactions into polymeric systems. The early efforts in the field were directed toward seeing what architectures are possible. In addition to the main-chain and side-chain supramolecular polymers discussed herein, we have demonstrated that the hydrogen bond mediated cyclic assembly of dendrimers and linear polymers (to make supramolecular stars) is feasible.^[57–61] The number of architectures available is limited only by the imagination of the researcher.

These early studies have established conclusively that noncovalent interactions, such as hydrogen bonding, metal coordination, π - π stacking, and electrostatic interactions, can be used to create new supramolecular polymeric architectures. Many of these studies have utilized hydrogen bonded complexes, because this particular noncovalent force has a number of advantages. These include the easy tunability of the strength of the complexes, the large number that has been studied, their frequent orthogonality, and the ability to reverse the binding in response to external stimuli like solvent, pH, and temperature.

In this mini-review, we briefly summarized the development of hydrogen bonding motifs and systems, which are often categorized by their number of hydrogen bonds. Thus, triply, quadruply, and sextuply hydrogen bonded complexes are the most studied and most frequently used in applications. We described their use in preparing two general types of supramolecular polymers: main-chain and side-chain functionalized. The research efforts described herein demonstrate the potential use of noncovalently assembled and/or functionalized polymers in the generation of unprecedented polymeric materials with a high degree of complexity that may find applications ranging from electronic devices to biomaterials. The key features of these polymers are their reversibility, which can produce recyclability and stimuli responsiveness.

One can imagine a wide range of applications, from thermoplastics that flow like water above a certain temperature, to materials that change their form in the presence of specific gases (e.g., auto-pressure-relieving vessels). What remains to be seen is whether these types of applications can indeed be realized with supramolecular polymers. The mechanical strength of main-chain polymers prepared from low molecular weight monomers may not have sufficient stability. Commercialization will also require recognition units that are both inexpensive to prepare and possess a chemical and thermal stability that makes them compatible with common polymer processing conditions. This latter aspect is one that requires more attention, and it is likely that a number of commonly used

modules may not be sufficiently stable at the high temperatures needed. Continuing studies in this area should rapidly move toward addressing some of these issues and exploring real applications. On a positive note, however, it is absolutely clear that the potential for a remarkably broad range of advanced materials appears to be almost limitless.

Acknowledgements

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