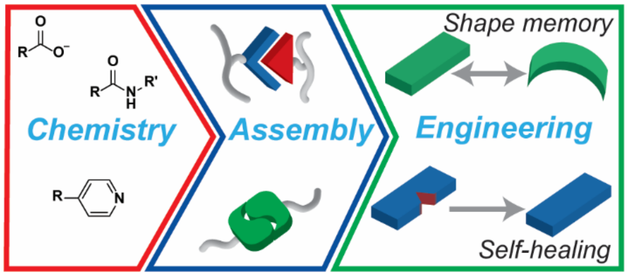
100th Anniversary of Macromolecular Science Viewpoint: Engineering Supramolecular Materials for Responsive Applications – Design and Functionality

Chase B. Thompson[a] and LaShanda T.J. Korley[a,b]*

Abstract

Supramolecular polymers allow access to dynamic materials, where non-covalent interactions can be used to offer both enhanced material toughness and stimuli-responsiveness. The versatility of self-assembly has enabled these supramolecular motifs to be incorporated into a wide array of glassy and elastomeric materials; moreover, the interaction of these non-covalent motifs with their environment has shown to be a convenient platform for controlling material properties. In this Viewpoint, supramolecular polymers are examined through their self-assembly chemistries, approaches that can be used to control their self-assembly (*e.g.* covalent crosslinks, nanofillers, etc.), and how the strategic application of supramolecular polymers can be used as a platform for designing the next-generation of smart materials. This Viewpoint provides an overview of the aspects that have garnered interest in supramolecular polymer chemistry, while also highlighting challenges faced and innovations developed by researchers in the field.



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Introduction

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[a] Department of Materials Science and Engineering, University of Delaware, 127 The Green, Newark, DE 19716, USA
[b] Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St, Newark, DE 19716, USA
* E-mail: lkorley@udel.edu

The development of the next generation of responsive polymeric materials requires systems that are both tough and functional, requiring dynamic materials capable of reacting to specific stimuli. Self-assembly and non-covalent interactions provide access to such materials through the growth of well-ordered supramolecular structures. These strategies are universally observed in biological systems, where the presence of self-assembling motifs offers a wide array of properties, from the toughness of mussel byssus threads to the responsive stiffness of the sea cucumber dermis.[1,2] In all cases, the properties of the self-assembled material are heavily impacted by the non-covalent architecture and their environment wherein careful balances are struck to ensure optimal self-assembly and stimuli-responsiveness.

In synthetic systems, supramolecular chemistry has been applied to incorporate these precise non-covalent interactions into macromolecular systems. In such cases, interaction type (hydrogen bonding, metal-ligand coordination, π-π stacking, *etc.*), self-assembling architecture, and material environment (*e.g.* polymer backbone polarity) are important parameters in establishing the nanoscale and bulk polymer behavior.[3,4] Significant research has been conducted to investigate the underlying structures that give rise to complex non-covalent assemblies as well as to how these structures can be controlled.[5–7] Through strategic manipulation of the system components, tough responsive materials have been constructed for applications in areas such as self-healing, sensing, and soft robotics.

In many cases, our ability to synthesize new supramolecular architectures has outpaced our understanding of the precise behavior that underpins their desired responsive nature. For instance, probing the dynamic response of these systems is difficult, especially in the case of elastomeric and glassy systems.[8] Another obstacle is the dependence of self-assembly on polymer architecture and the interaction of the supramolecular motif with the backbone; due to the flexibility of polymer core chemistries *(e.g.* polar vs. non-polar backbones), conjugation strategies, and the potential presence of additives and fillers, the field of supramolecular polymer elastomers and glasses has grown exceedingly complex. Nevertheless, significant progress has been made in understanding self-assembly through strategic material design.[9–12]

In this Viewpoint, we focus on recent advances in the development of glassy and elastomeric supramolecular polymeric systems, particularly the ability to control the self-assembly process to yield precise dynamic material systems while accounting for the convoluted secondary interactions between the supramolecular motif and the polymer backbone, monomer unit friction, *etc*.[8,13] We examine the design of supramolecular polymers by discussing differences in interaction type and polymer architecture (*e.g.* telechelic *vs.* pendent supramolecular functionalization). Then, the engineering of supramolecular polymers to elicit specific mechanics and stimuli-responsive behavior is discussed in-depth to shed light on how these material platforms can be controlled. Finally, the application of these dynamic materials in the design of functional polymeric devices is examined to understand how the structure-property relationships of the self-assembled polymer contribute to the function of the device. While supramolecular self-assembly has also been extensively investigated in the design of hydrogels,[3,14,15] supramolecular single-chain polymer nanoparticles,[16] and extensive solution-based supramolecular polymer arrays,[5,17] this Viewpoint solely focuses on materials and devices derived from supramolecular elastomers and glasses.

Supramolecular Polymer Design – Building and Understanding Non-Covalent Interactions

At a basic level, the chemistry and structure behind a supramolecular motif control much of its character, including the association type, assembly architecture (*e.g.* chain extension, lateral stacking), and interaction specificity.[5,14] Such parameters are programmed into the supramolecular motif during synthesis, and these behaviors are generally identified through extensive material characterization. However, the evolving design of supramolecular polymers offers important insight into how these assemblies can be controlled by means of careful fabrication.

Hydrogen bonds. Out of the many non-covalent interaction types available for material fabrication, hydrogen bonding has dominated the field due to its simple design and ease of tuning interaction architecture and specificity.[4,18] In nature, these interactions are prominent, contributing to the stabilization of common peptide secondary structures such as α-helices and β-sheets, wherein the application of multiple hydrogen bonds across a single molecule assists in generating stable self-assembled structures.[3,19] Commonly, amide, urethane, and urea bonding arrays are utilized in hydrogen bonding systems due to the inherent presence of a specified hydrogen bonding donor (N-H) and hydrogen bonding acceptor (C=O) in these functionalities.[4] Moreover, the number of hydrogen bonding units and the arrangement of these donor and acceptor sites in relation to one another greatly impact the association behavior of the supramolecular motif, which is tied to material mechanics, temperature sensitivity, and stimuli-responsive behavior.[18] In one example, the association strength of triple hydrogen bonding arrays was studied, where changes in the order of hydrogen bonding donor (D) and acceptor (A) sites along the molecules resulted in substantial changes in the association constant (K_a). The K_a of the DDD and AAA dimers was shown to be substantially higher than that of the DAD and ADA hydrogen bonding arrays.[20,21] This observed response can be attributed to secondary electrostatic interactions occurring along the molecule; the partial positive and negative charges that rest on the hydrogen atoms and oxygen or nitrogen atoms, respectively, repel neighboring groups with the same partial charge. In supramolecular motifs where these neighboring electrostatic charges are favorable, K_a values are higher than in cases where the charges repel. Such secondary aspects of hydrogen bonding motifs are important strategies in supramolecular material design, allowing for tunable assembly behavior with only slight shifts in chemical structure. Increasing or decreasing the number of hydrogen bonding sites in a supramolecular motif also offers opportunities to modulate the assembly strength; as such, a number of supramolecular chemistries have arisen bearing anywhere from two hydrogen bonding sites (*e.g.* adenine/thymine) to as many as six hydrogen bonding sites (*e.g.* barbituric acid/Hamilton wedge) between complementary molecules (**Figure 1**).[4,18,21–24] Further tunability is obtained by employing self-complementary or complementary hydrogen bonding motifs. In self-complementary systems, specific hydrogen bonding occurs between a single species, such that the supramolecular polymers spontaneously assemble; complementary hydrogen bonding interactions occur between A and B type supramolecular species, introducing stoichiometric dependence into the system, where changes in the ratio of A:B can be used to tune dynamic bonding in the material.[4,22,25]

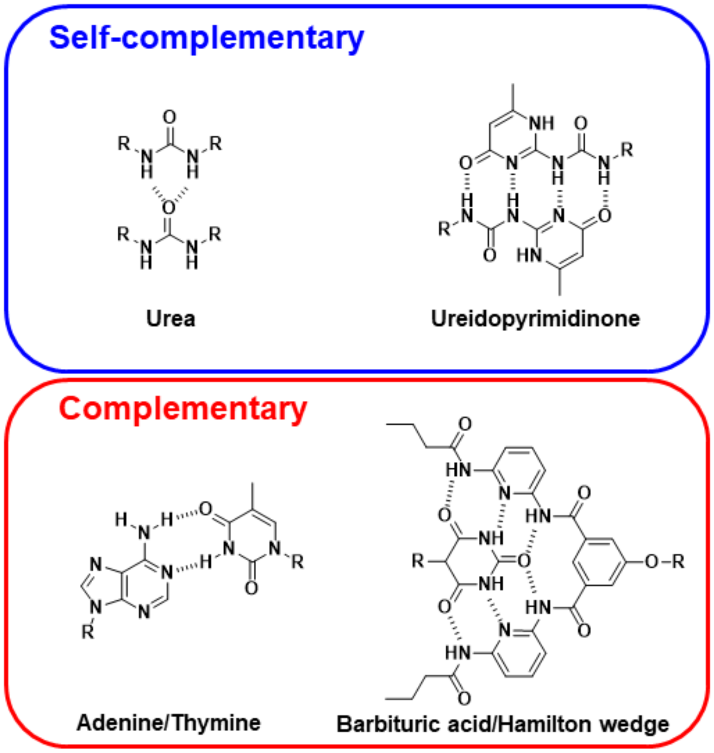

Figure 1: Examples of self-complementary and complementary hydrogen bonding supramolecular motifs.

In seminal work towards designing a versatile hydrogen bonding motif, Meijer and co-workers developed a quadruple hydrogen bonding synthon, 2-ureido-4[1H]pyrimidinone (UPy), that displays a unique donor-donor-acceptor-acceptor (DDAA) array.[26,27] The potential for favorable cross interactions between the two central donor and acceptor sites and the high number of hydrogen bonding sites gives rise to strong dimerization ($K_a \sim 10^7$ M^{-1} in chloroform).[27] The simple synthesis and strong binding of UPy motifs have made it a popular motif to introduce self-assembly into polymers. It has, in many ways, become a workhorse in the field of supramolecular polymer materials due in part to the ease of conjugation of the existing UPy monomer species to a wide range of polymeric cores, which include reactive vinyl groups, free isocyanates, and blocked isocyanates.[28–30] The generation of new materials utilizing UPy has therefore become a convenient platform for understanding the formation of hierarchical, hydrogen-bonded supramolecular structures.

As with most types of non-covalent interactions, hydrogen-bonded supramolecular polymers are sensitive to their environment, such as the identity of the polymer core to which they are attached. In many cases, hydrogen bonding motifs are conjugated to hydrophobic polymer cores; these neutral cores promote phase separation of the non-covalent moiety, which can assist in the organization of supramolecular motifs during film formation.[31] Conversely, the use of polar polymers can introduce competitive hydrogen bonding, which can disrupt of the organization of supramolecular groups. The presence of ether linkages, hydroxyl groups, and other polar functionalities have been shown to disrupt the organization of UPy motifs.[32–34] While largely seen as detracting from supramolecular polymer properties, these competitive interactions can be used to modify supramolecular properties for desirable outcomes. For instance, Weder *et al*. utilized the competitive interactions between oligo(propylene glycol) and UPy to synthesize a versatile supramolecular methacrylamide monomer.[35] The intramolecular interactions between UPy and the polar oligo(propylene glycol) core disrupted supramolecular ordering and resulted in a liquid monomer as opposed to the solid UPy (meth)acrylate-type monomers that are typically reported in literature;[36,37] this viscosity tuning enabled the authors to copolymerize the supramolecular monomer with commercial acrylates in the bulk while maintaining increased mechanics dictated by the UPy motif. As such, the chemistry of the supramolecular polymer core or other constituents within the system must be considered during material design, as they can detract from a system’s self-assembly or, if utilized appropriately, add another level of tunability to the self-assembly. The quadruple hydrogen bonding UPy supramolecular motif has become one of the most widely used non-covalent bonding chemistries which can be explained by its ease of synthesis and strong self-complementary interactions.[4] While UPy is a dominant hydrogen bonding synthon, other strongly hydrogen bonding supramolecular groups, such as the dimers formed by the nucleic acid residues adenine and thymine, and the Hamilton wedge and barbituric acid (**Figure 1**), are equally capable of forming dynamic supramolecular materials. Moreover, their shifts in K_a when compared to UPy allow for a diverse library of interaction strengths, offering tunable dynamics that can be used to control bulk material mechanics or stimuli-responsive behavior.[8,11,38] For instance, films consisting of barbituric acid-functionalized poly(n-butyl acrylate-*block*-styrene-*block*-n-butyl acrylate) were crosslinked with Hamilton wedge-telechelic poly(isoprene) were shown to exhibit high interaction strength ($K_a \sim 5.13 \times 10^4$ M^{-1}) that allowed them to form tough, healable materials.[39] This Viewpoint strives to highlight the diversity of supramolecular polymers formed using different non-covalent chemistries.

Metal-ligand coordination. In terms of interaction strength, tunability, and responsiveness, few non-covalent interaction types can compete with metal-ligand coordination. While not as prominent in nature as hydrogen bonding, coordination interactions play an important in role in the structural stability of many invertebrates. For instance, the byssal threads of marine mussels rely heavily on coordination interactions between catechol groups and Fe^{3+}, and histidine and Zn^{2+} to act as sacrificial bonds while adhered to rocks or other surfaces in intertidal zones.[2,40] In this case, the reversible rupture of the non-covalent interactions release energy during deformation, preventing catastrophic failure and allowing recovery of the reversible bonds for multiple deformation cycles. Metal-coordinated self-assembly has garnered interest for the design of supramolecular materials due in part to its roles in biological systems as well as the ability to tailor self-assembly by varying the identity of the coordinated metal.

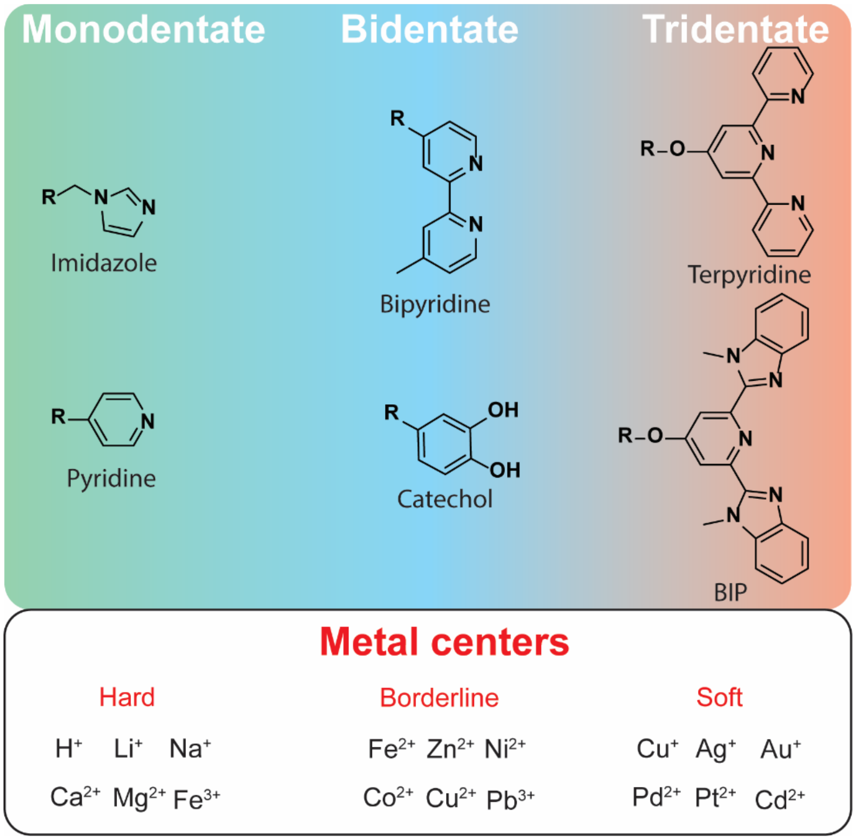

Figure 2: Common metal-coordinating supramolecular motifs and classification of metal centers using hard-soft acid base theory.[41,42]

The interaction strength in metal coordination is determined by the identity of both the metal center and the ligand. In both cases, the interactions that occur between a metal and a ligand are dictated by the polarizability of the molecules.[41] Metal centers, which act as Lewis acids, can be more or less polarizable, which results in a loose categorization as 'soft' or 'hard', respectively (**Figure 2**). Hard Lewis acid metals include species such as Li^+ and Ca^{2+}; these are generally smaller and not easily polarized.[41,42] On the other hand, softer metal centers, such as Cu^+ and Pd^{2+}, are larger, and their electron clouds are more easily deformed. Borderline metal centers, which lie between hard and soft Lewis acids, include Zn^{2+} and Cu^{2+}. These borderline Lewis acid species tend be fairly deformable and, when mixed with appropriate ligands, tend to form highly dynamic coordination interactions.[42]

Ligands, which are classified as Lewis bases, follow a similar classification to their metal counterparts. Hard bases, such as NO_3^-, typically exhibit a high electronegativity and small size, while their soft ligand counterparts have intermediate electronegativity and larger size, including CO and CN^-.[41,42] Complexes between hard acids and hard bases lead to ionic interactions, while soft bases and acids instead form covalent-like bonds. Borderline ligands, which include compounds such as pyridines and sulfates, exhibit properties that lie between hard and soft bases and tend to induce dynamic complexes that lie between ionic and covalent character.[41] It has been shown that, regardless of the employed ligand, the stability of complexes incorporating divalent metals nearly always follows the Irving-Williams series: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Fe^{2+} < Cu^{2+} > Zn^{2+}$, which mirrors the first row of divalent transition metals; the stability of Zn^{2+} complexes has been shown to be roughly equivalent to that of Co^{2+} complexes in many cases.[43,44] When paired with appropriate ligands, these complexes share electrons and form bonds that are similar to covalent bonds, although generally weaker and, as a result, more dynamic.[45] Furthermore, the identity and charge on the metal center dictates the coordination geometry of the supramolecular complex, promoting shifts in supramolecular structures as a function of the choice of the metal center. The choice of coordinating metal salt is further complicated by the identity of the counterion. This influence was demonstrated by Bao *et al.* where the use of more strongly coordinating Cl^- compared to a weakly binding triflate counteranion led to disruption of the self-assembled polymer through competitive coordination to the metal center.[46]

The metal center is bound to a polymer chain through their interaction with functional ligand motifs. Popular binding chemistries include pyridine and imidazole groups (**Figure 2**).[41,47,48] The rigidity of aromatic groups, such as pyridines, allows for increased specificity and directionality of the coordination chemistry, while the presence of accessible electron lone pairs on functional groups such as aryl amines allows them to form bonds with the cationic metal center.[41] Beyond the choice of ligand chemistry, the number of coordination sites on the ligating molecule will also determine binding strength. In general, bi- and tridentate ligands will offer higher binding affinity than monodentate ligands, which adds another layer of assembly control during materials design.[49] The intermediate binding strengths of such supramolecular complexes, which generally makes them stronger than hydrogen bonding motifs,[14] offer a wide array of tunability in the resulting metallopolymer systems.

In natural materials, a common metal-coordinating ligand is the imidazole residue on the amino acid histidine.[2,45,50,51] Coordinated histidine plays an important role in the toughening of mussel byssus threads and polychaete worm jaws, where Zn^{2+}-coordinated histidine act as sacrificial bonds and crosslink junctions.[45,52–54] While the imidazole groups on histidine residues are more weakly binding monodentate ligands, their ability to exchange rapidly and to form coordinated clusters around metal centers provides opportunities for developing synthetic supramolecular materials.[49,55] Histidine-derived polymers have been studied as model self-healing materials, where it was shown that both the presence of protecting groups on the imidazole ring and the identity of the counterion for Zn^{2+} salts dictated the association strength and coordination stoichiometry.[56] Self-assembly in these systems could be further refined with the addition of a small amount of aspartate functionality in the polymer backbone, which lowered the binding affinity of the metal for the polymer chains and resulted in better healability, possibly due to the increased mobility of the metal centers.[57]

The versatility of histidine and histidine-mimetic chemistries has made them attractive platforms for tuning material properties by relying on the dynamic and relatively weak binding of the imidazole group. Guan *et al.* used a histidine-mimetic imidazole acrylate monomer (IMZa) to introduce metal-ligand coordination interactions into photopolymerized elastomers (**Figure 3A**).[58] To mimic the gradients in metal-coordination crosslinks exhibited in the jaws of polychaete worms,[45,52] the authors introduced gradients into the imidazole-containing network (ICN) by slowly drawing the film out of an acetonitrile solution containing metal salts; simultaneously, a syringe pump charged more metal salts into the solution to encourage the formation of additional coordination bonds in the film.[58] As a result, the ICN films showed changes in the local Young's modulus that corresponded well with changes in the local mol% of metal as measured by X-ray photoelectron spectroscopy (XPS) (**Figure 3B** and **3C**), where an increased local concentration of metal centers corresponded to stiffer areas of the films.

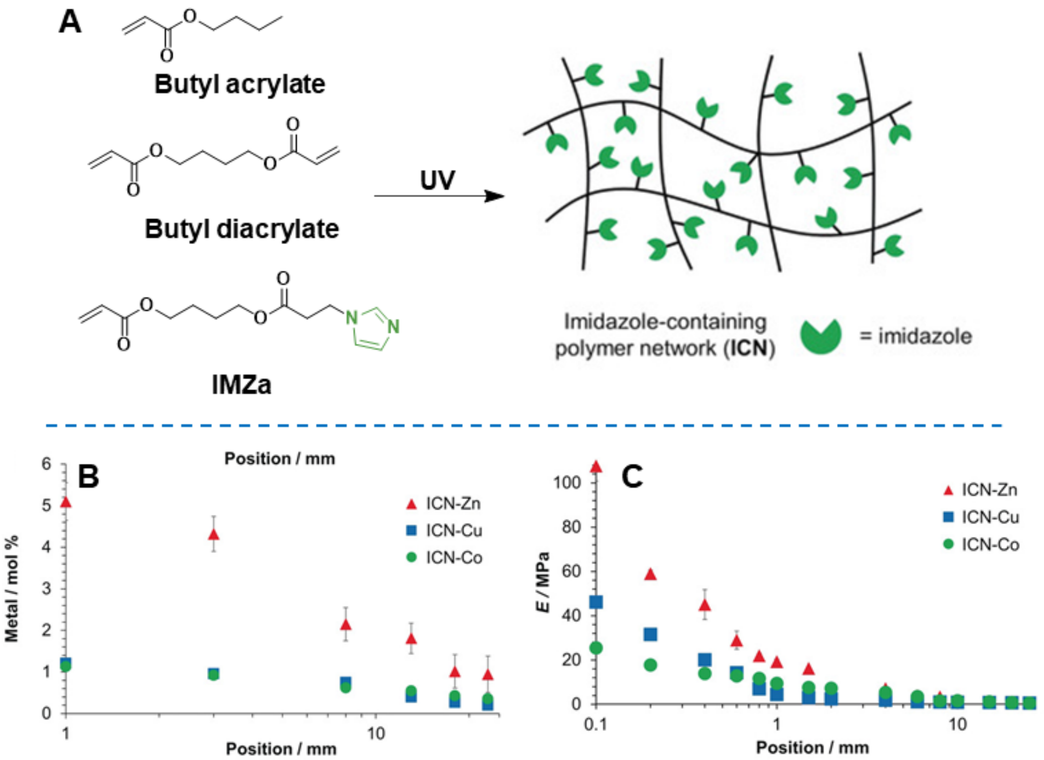

Figure 3: A) Monomer structures used in the photopolymerization of ICN films. B) Amount of metal (relative to O, C, and N) along lateral axis of film after gradient formation. C) Young's modulus of ICN films down the lateral axis demonstrating how changes in local metal concentration dictate film stiffness. Adapted with permission from ref. 58. Copyright 2017 John Wiley & Sons.

Hydrophobic interactions and π-π stacking. While the field of supramolecular self-assembly has been traditionally dominated by hydrogen bonding and metal-ligand coordination interactions, hydrophobic interactions and π-π stacking have found several niche applications in the production of glassy and elastomeric materials. In most cases, these interactions are generally a secondary means of self-assembly that assist in reinforcing and stabilizing supramolecular assemblies formed by other, stronger associative interactions. For instance, the presence of lateral π-π stacks aids in strengthening of the hydrogen bonded UPy motifs, forming more ordered systems.[59,60]. Similarly, hydrophobic interactions can contribute to the shielding of sensitive supramolecular moieties from competitive interactions, which allows polar or complex polymer cores to be used without disrupting the main means of self-assembly.[32] In such cases, the presence of these secondary non-covalent interactions are an important aspect in self-assembly of other moieties.

While generally a secondary consideration in the design of supramolecular polymers, hydrophobic and π-π stacking interactions can be utilized as primary avenues for directed self-assembly as well. Reinforced elastomers built from hydrophobic interactions have been constructed utilizing host-guest interactions between cyclodextrin (CD) motifs and appropriate guests to interact with the hydrophobic pocket. Typically, CD host-guest complexes exhibit low association strength while allowing for several types of guest molecules to fit into the hydrophobic pocket, including benzene rings and adamantyl groups.[14,61,62] Such materials typically exhibit high extensibility when paired with comonomers displaying low glass transition temperatures (T_g), although their behavior can be modified through the incorporation of hydrogen bonding comonomers or guest molecules with a strong binding constant.[62–64] It is worth noting that, while hydrophobic interactions and π-π stacking are not common motifs for the construction of elastomers, these interactions also are common in the synthesis of responsive hydrogel materials, which are outside the scope of this article.[3,62,65]

Beyond the base supramolecular chemistry, placement of the non-covalent binding motif on a polymer backbone has a strong impact on how self-assembly occurs and the manner in which the material will behave as a result. Generally, supramolecular polymers are categorized into three architectures: 1) telechelic, wherein the supramolecular groups are attached to the chain ends of the prepolymer, 2) chain-centered, where the supramolecular motifs are embedded into the polymer backbone, and 3) pendent, where the supramolecular motifs are attached to side chain groups on the polymer core (**Figure 4**). While these chain attachment schemes denote the primary types of supramolecular polymers, a more complete picture is illustrated by examining how chain placement can be used to control the supramolecular assembly to result in a diverse library of materials.

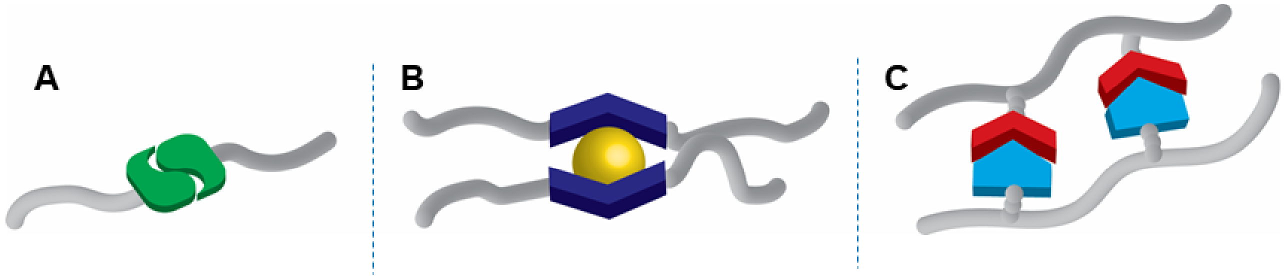

Figure 4: Depiction of (A) a self-complementary telechelic supramolecular polymer, (B) a chain-centered supramolecular polymer, and (C) a complementary pendent supramolecular polymer architecture.

Telechelic supramolecular polymers. Telechelic supramolecular systems are a commonly applied polymer architecture, allowing for a simple starting material to construct a more complex system through the self-assembly of functional end-groups. In most cases, the reactive core consists of an oligomer, with number average molecular weights (M_n) generally lying between

1000-5000 g/mol.[27,60,66–68] This molecular weight range offers a higher concentration of supramolecular end groups when compared to large polymer cores. It also serves to minimize chain entanglement, ensuring a low viscosity melt for ease of processing and preventing interruption of self-assembly during film formation.[69] However, higher molecular weight polymer backbones also have been utilized when designing telechelic supramolecular polymers, especially to access specific architectures, such as supramolecular polymer grafted nanoparticles or as functional grafts for forming supramolecular polymer brushes; such strategies sacrifice a high concentration of supramolecular groups beneficial to tough material fabrication for precise dynamic structures.[70–73]

Since chain-end functionality is required, polymers built by step-growth or ring opening polymerization methods are common cores.[27,59,74–76] Common polymer backbone chemistries include poly(ε-caprolactone) (PCL) and poly(tetrahydrofuran) (PTHF), but other cores such as block copolymers, silicones, and trimethylene carbonates have been utilized as well, showcasing the versatility of this architecture.[29,60,74–78] As a common model material, non-polar oligomeric cores, such as poly(ethylene-*co*-1-butene) (PEB) and poly(butadiene) (PB), encourage phase separation and organization of non-covalent motifs, allowing for the growth of extensive supramolecular aggregates and facilitating the formation of tough supramolecular materials.[27,68,79–81]. The supramolecular motif is commonly attached to the oligomer through post-polymerization modification, where the polymer end groups are coupled to non-covalent groups through a variety of chemistries, such as isocyanate coupling, esterification, or ‘click’ type reactions.[27,82–84] The attachment of supramolecular motifs also can be achieved for cores synthesized *via* controlled radical polymerization routes, such as atom transfer radical polymerization (ATRP), reversible-addition fragmentation chain transfer polymerization (RAFT), and ring-opening metathesis polymerization (ROMP) through either chain-end modification or through the design of supramolecular-functional initiators or chain transfer agents.[85–88] This strategy has the advantage of ensuring all of the polymer chains contain a supramolecular group on their chain end, which can be a shortcoming of post-polymerization modification where some end groups will be left unreacted.[85] The chemical flexibility of polymer cores allows for the control of self-assembly by tuning the backbone's chemistry. Rowan and co-workers demonstrated how this control can be realized by inserting a metal-coordinating tridentate ligand, 2,6-bis(1'-methyl-benzimidazolyl)-4-hydroxypyridine (BIP), on the chain ends of either polar PTHF or non-polar PEB (**Figure 5A**).[76] When the supramolecular polymers were coordinated with $Zn(Ntf_2)_2$, the more non-polar PEB core promoted phase separation and self-assembly of the BIP motifs, while the ether linkage in the PTHF core competitively bound the Zn^{2+}, a consequence of phase mixing. Small-angle X-ray scattering (SAXS) showed an increase in peak width and a decrease in lamellar ordering in the PTHF cores when compared to the PEB; this decrease in order was accompanied by a reduction in the mechanics of the PTHF-based material when compared to the PEB core (**Figure 5B and 5C**). This shift in assembly provided a convenient handle for modulating the final properties of the supramolecular elastomer.

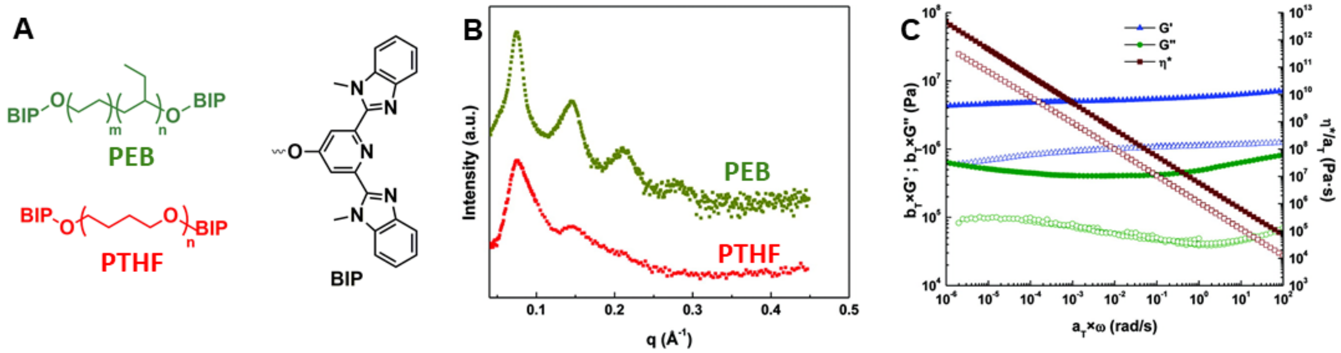

Figure 5: A) Non-polar PEB and polar PTHF cores and metal-coordinating BIP ligand. B) 1D SAXS patterns of PEB- and PTHF-based Zn-coordinated supramolecular polymers, showing the

disruption of long-range ordering when PTHF is employed as the polymer backbone. C) Rheological master curves of Zn-coordinated supramolecular polymers containing the PEB (filled) or PTHF core (unfilled). Adapted with permission from ref. 76. Copyright 2012 American Chemical Society.

In many cases, telechelic supramolecular polymers are constructed using polymeric or oligomeric cores exhibiting a low T_g to enhance chain mobility of the resulting self-assembled elastomer, allowing for enhanced supramolecular bond exchange and processability. However, the use of glassy polymer backbones also has attracted attention due in part to the opportunity to improve the overall stiffness of the supramolecular material while maintaining the energy dissipation and enhanced toughness offered by non-covalent bonds.[74,89] Below the T_g, polymer chain mobility is limited, however, supramolecular motifs still have been shown to contribute to the bulk material behavior in this state. Utilizing dielectric relaxation spectroscopy (DRS) and dynamic mechanical analysis (DMA), Sijbesma *et al.* demonstrated that relaxation processes associated with the exchange of UPy dimers were present in a system below its T_g.[90] Moreover, the relaxation of UPy groups measured experimentally outpaced the relaxation times predicted using DRS; this was rationalized by the UPy groups being unable to sample larger areas for relaxation and, as a result, dimer exchange reached a local equilibrium more quickly than if the UPy groups were allowed to experience a larger area of the network.

Chain-centered supramolecular polymers. If additional control over molecular weight is desired without sacrificing the concentration of supramolecular motifs, a chain-centered supramolecular platform offers the ability to incorporate non-covalent motifs into the polymer backbone, where they behave as well-defined ‘hard’ segments separated by a flexible polymer soft segment. In this case, di- or multi-functional supramolecular groups are reacted with telechelic prepolymers in a chain extension process; the main chain assembly of the supramolecular moieties results in the formation of physical crosslinks between chains.[10,91] When compared to telechelic supramolecular polymers, these chain-centered architectures typically enhance phase mixing, which can be attributed to the reduced mobility of the supramolecular groups due to their direct incorporation into the polymer backbone.[92]

The presence of these 'hard' and 'soft' segments in chain-centered polymers draws parallels to the structure of conventional polyurethanes, where phase separation and organization of the hard segments creates a tough, physically crosslinked network.[93] A polyurethane framework has been adapted to contain a metal-coordinating motif into the polymer backbone.[94] The organization of the supramolecular polymer increased hydrogen bonding between adjacent hard segments and encouraged shifts in material mechanics, where the strong coordination of the metal-ligand supramolecular motifs was linked to enhanced stability of the hard segments during heating and deformation.

Pendent supramolecular polymers. Whereas the concentration of supramolecular groups is dictated by the backbone molecular weight in telechelic supramolecular polymers, materials containing supramolecular motifs pendent to the polymer backbone have much more synthetic flexibility. Generally, the supramolecular motif is attached to a reactive monomer base (*e.g.* acrylates, norbornenes) and polymerized in the presence of suitable initiators and comonomers.[88,95–97] The tunability of the polymer feed offers incredible versatility to the pendent architecture platform. Such polymers have been formed through a number of polymerization techniques including ATRP. RAFT, and ROMP.[87,88,98,99] The adaptability of using a supramolecular monomer of this type allows for thermal response tuning, such as modification of the T_g , simply by changing the identity of the comonomer.[100–102] Moreover, the supramolecular motifs can be incorporated into polymer brushes or confined to a single segment of a block copolymer, providing many avenues for controlled assembly.[49,99,103–105]

Supramolecular Polymer Engineering – Controlling Self-Assembly through Molecular Ordering and Secondary Interactions

While the synthesis of supramolecular polymers itself is an important aspect of fabricating versatile materials derived from tunable assemblies, it is but one facet of these systems. The choice of chemical constituents can have important impacts on the processing of such materials, such as how the supramolecular assemblies interact with other polymer properties including crystallinity or the presence of covalent crosslinks. In this section, the interaction of self-assembled networks with other material features and components is explored to understand how self-assembly can be controlled through these polymer architectures and secondary interactions.

Covalent crosslinks. One route to tune self-assembly is by overlaying covalent crosslinks onto the supramolecular structure. In traditional supramolecular polymers, the dynamic exchange of assembled non-covalent motifs leads to significant stress relaxation in supramolecular materials; this behavior is driven by the release of stored energy—or stress—by dissociation and reassociation of the supramolecular motifs when the material is held under tension.[106] Permanent crosslinks restrict this behavior; when added into a supramolecular network, these covalent junction points can hinder stress relaxation events that occur in the supramolecular phase.[37,107,108] The incorporation of covalent crosslinks into transient supramolecular materials also has been shown to increase the activation energy of associated non-covalent networks, decreasing the amount of energy loss caused by partner exchange.[109] This decrease in mobility and supramolecular exchange is a result of the constraining covalent network, where the confining permanent crosslinks increase the potential for a dissociated supramolecular group to associate with its original partner, preventing energy loss.[81,110,111] Concomitantly, this network confinement has also been shown to increase the dissociation temperature of the supramolecular network, leading to more thermally stable assemblies.[81] This cooperativity between a permanent and transient network offers enhanced stress recovery after a deformation cycle. During deformation, the transient supramolecular network dissipates energy; after release, the elastic permanent network that tethers polymer chains together will pull the network mesh into its original shape, facilitating the recovery of the supramolecular bonds that reinforce the material.[108] This interplay allows for the network to display its original mechanics upon subsequent deformation cycles after a brief recovery period.

These dually-crosslinked networks have seen broad application as shape memory materials.[112] In such systems, a reversible crosslinking mechanism acts as a switching point, allowing for fixation of a temporary material shape after stimulus exposure.[112] In contrast, a crosslink junction, or net point, serves to 'pull' the network back into its original shape when the fixed-shape material is exposed to a proper stimulus. The strength and specificity of supramolecular interactions make them optimal switching points. By changing the supramolecular interaction type and architecture, different response profiles can be achieved. Generally, the application of hydrogen bonding supramolecular motifs results in highly temperature-sensitive shape memory materials.[100,113] In other cases, metal-ligand coordination interactions have been employed to develop both photo- and chemoresponsive shape memory platforms.[80]

While many examples of supramolecular polymer networks containing permanent crosslink junctions are formed from dually-crosslinked single networks (SN), where supramolecular interactions and covalent crosslinks co-exist on a polymer chain, interpenetrating networks (IPNs) provide another architecture by which the presence of permanent crosslink junctions can be used to tune supramolecular dynamics. Traditional IPNs consist of two or more orthogonal networks crosslinked in the presence of one another without chemical linkages between the phases.[114] In this way, the formation of covalent crosslinks arrests phase separation and forces interactions at the phase interface, leading to a material with smaller microphase-separated morphologies and increased stress transfer between phases during deformation.[115–117] If this stress is transferred to a dissipating network, such as a supramolecular polymer system, the energy associated with the deformation can be efficiently released. These interactions between phase boundaries have proven to be particularly important in microphase-separated IPN frameworks. In one example from our own group, the presence of favorable hydrogen bonding between quadruple hydrogen bonding UPy-functionalized PEB and a covalently crosslinked hydroxyl-terminated PB phase resulted in marked increases in material toughness when compared to semi-interpenetrating networks (SIPNs) made with alkyl-terminated PB.[66] Similarly, interfacial interactions between covalently crosslinked poly(ethylene glycol)dimethacrylate (PEGDMA) and a Zn^{2+}-coordinated supramolecular polymer were shown to dictate self-assembly of the non-covalent motifs, where competitive interactions between oxygen units along the PEGDMA backbone and the coordinated supramolecular arrays decreased the overall order within the supramolecular phase as probed *via* SAXS.[118] The presence of these interactions between phases are important considerations when designing microphase-separated materials such as supramolecular IPNs.

While the use of covalent crosslinks in tandem with supramolecular interactions is a convenient platform for tuning self-assembly, the use of permanent crosslinks prevents reprocessability of these materials. This issue can be avoided by combining the supramolecular interactions with dynamic covalent crosslinks, where the creep resistance of a covalently crosslinked network is maintained, while still allowing materials to be reprocessed or healed after fracture. Common dynamic covalent chemistries that can be used for this platform include Diels-Alder, boronate esters, and imine adducts.[119,120] The Konkolewicz group, for instance, has combined acrylate-functional UPy (UPyA) and furan-maleimide diacrylate (FMIDA) (a Diels-Alder adduct) monomers to form both SN and IPN-based architectures that contain both non-covalent and dynamic covalent pendant crosslinks (**Figure 6**).[33,37,98,107] Interestingly, the single networks are more creep resistant than the corresponding IPN materials; this behavior can be attributed to the orthogonal IPN architecture allowing for more dissipative exchange behavior between UPy dimers to occur.[107] This response is also apparent in the mechanics of the IPN when compared to the single network material (**Figure 6A and 6B**). The greater mobility and energy dissipation available to the IPN promotes enhanced extensibility and a higher overall fracture energy, demonstrating the trade-off between creep resistance and bulk mechanics when shifting between SN and IPN architectures.

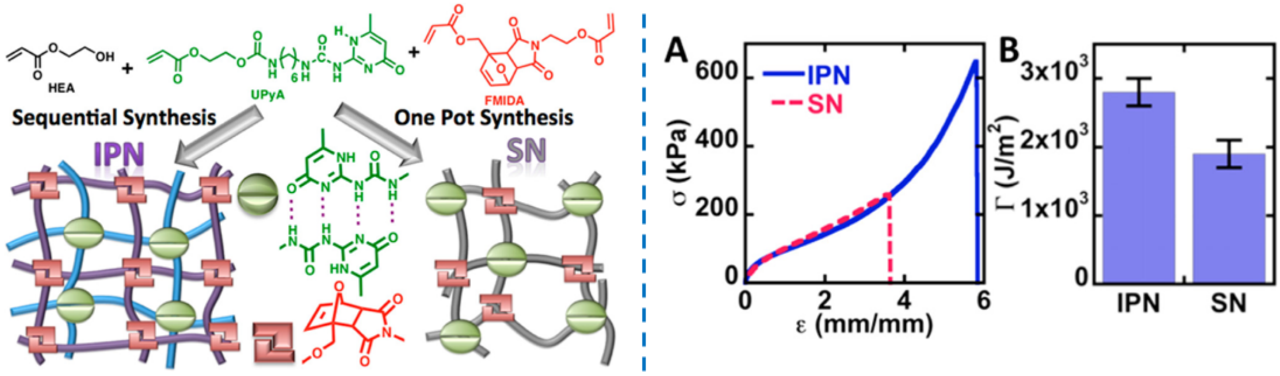

Figure 6: (Left) Scheme for the formation of SN and IPNs containing both supramolecular and dynamic covalent crosslinks. (Right) Tensile behavior (A) and corresponding fracture energy (B) of the IPN and SN samples. Adapted with permission from ref. 107. Copyright 2017 American Chemical Society.

Covalent crosslinks have proven to be an effective platform for modifying self-assembly behavior in supramolecular polymers. Great strides have been made in designing and understanding how covalent crosslink chemistry and network architecture (SN *vs.* IPN) can be utilized to limit creep compliance or enhanced material toughness, while maintaining stimuli-responsive behavior that offers access to shape memory or self-healing behavior. One interesting facet of covalent crosslinks that is especially apparent in IPNs is that the order of network formation matters; the first network, when swollen by the second, tends to be under more tension and acts sacrificially.[114,121,122] The impact of the order of network formations presents another handle for controlling self-assembly behavior, but, consequently, adds another layer of complexity to what are already complex systems. These architectural aspects, compounded with the breadth of chemistries available to supramolecular systems, offer a range of pathways to further tailor dynamic behavior in these materials.

Supramolecular polymer blends. In commercial settings, tuning of polymer properties are often achieved via the formation of a polymer blend, where two or more different polymers are mixed to yield a desirable combination of properties. However, many polymers do not form miscible blends which can be partially ascribed to the low increase in entropy during mixing of these high molecular weight materials; as a result, many polymer blends exhibit phase separation due to this immiscibility.[123] The shape and size of a phase-separated domain in a polymer blend are a determining factor of thermomechanical properties, and, as a result, controlling phase morphology or increasing material miscibility has become an important topic for fabricating more versatile blend material platforms.[124,125] The application of self-assembly to polymer blends serves as a means of 'bridging' immiscible polymer cores through favorable non-covalent interactions.

In many polymer blends, miscibility can be driven by favorable non-covalent interactions. This technology is commonly applied to complementary supramolecular interactions to drive interactions between the immiscible polymer cores. Applied supramolecular interactions include the use of adenine-thymine base pairs,[126] π-π stacking pincer-type interactions,[127] and Lewis pairs.[128] The tunable properties of such supramolecular systems have been used to fabricate self-healing systems and to enhance the properties of photovoltaic systems.[127,129] Moreover, the use of supramolecular polymer blend platforms has shown advantages over random copolymers derived from the constituent polymers and decorated with supramolecular functionality.[130] When blending two separate supramolecular polyesters consisting of PCL and poly(valerolactone) (PVL) backbones compared to samples made from their supramolecular random copolymer counterparts, the supramolecular blends were capable of assembling to maintain the crystallinity of the different polyester segments, allowing for greater control over thermal properties.[130]

Binder *et al.* demonstrated the importance of end group chemistry for forming miscible supramolecular blends of poly(isobutylene) (PIB) and poly(ether ketone) (PEK) using either thymine/2,6-diaminotriazine dimers ($K_a \sim 800\ M^{-1}$) or Hamilton wedge/barbituric acid interactions ($K_a \sim 3 \times 10^4\ M^{-1}$) (**Figure 7A**).[131,132] BCP1, consisting of thymine and 2,6-diaminotriazine functional PEK and PEB, respectively, formed stable, microphase-separated materials at room temperature as viewed by SAXS.[131] Upon heating, the domain-spacing (*d*) between scattering centers increased, corresponding the formation of larger phase separated domains (**Figure 7B**). Up until 145 ˚C (~ T_g of PEK), this increase in phase size was reversible; above this temperature, irreversible macrophase separation occurred. Conversely, BCP2 and BCP3, bearing the stronger binding Hamilton wedge/barbituric acid dimer, were stable to higher temperatures, only exhibiting a slight increase in *d* above 150 ˚C and complete macrophase separation at 230 ˚C. This example highlights that the choice of supramolecular interaction strength is a determining factor in the thermal stability of supramolecular polymer blends.

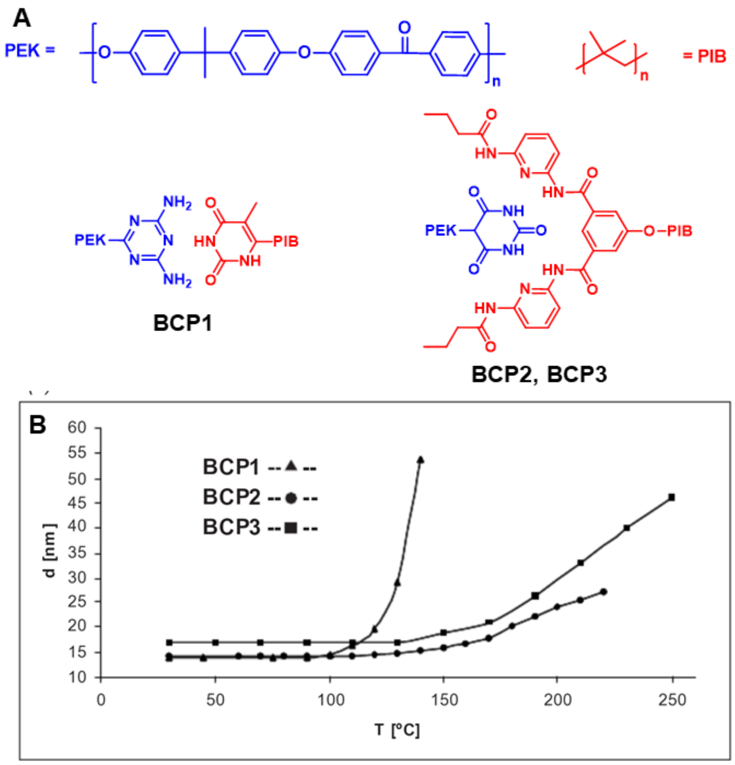

Figure 7: A) Structure of supramolecular PEK and PIB polymer blends. The functional PEK used in BCP3 has a slightly higher molecular weight (M_n ~ 5450 g/mol) than BCP2 (M_n ~ 4560 g/mol). Adapted with permission from ref. 131. Copyright 2005 John Wiley & Sons.

While blends are often constructed from supramolecular polymers containing different backbone identities, blends of supramolecular polymers can also be fabricated from systems containing orthogonal self-assembling motifs as a means of tuning the dynamic properties of the material, such as stimuli responsive behavior. For example, Weder *et al.* designed blends of trifunctional poly(propylene) (PPO) cores decorated with either hydrogen bonding UPy or Zn^{2+}-coordinated BIP supramolecular motifs (**Figure 8A**).[133] Blends of these two supramolecular PPO materials assembled orthogonally into nanophase-separated domains. The supramolecular phases also displayed unique stimuli-responsive behavior, where the UPy motif exhibited a lower melting temperature (~110 ˚C) than the assembled BIP (~ 240 ˚C), but the BIP phase could be disrupted by a competitive ligand, N,N,N’,N’-tetramethylethylenediamine (TMEDA). Using these different thermo- and chemo-responsive behaviors, these nano-assembled supramolecular blends exhibited triple shape memory behavior; in this case, both supramolecular phases served as distinct switching points for fixing temporary shapes due to their orthogonal responsivity (**Figure 8B**). Utilizing blends of supramolecular polymers is a powerful platform for improving miscibility of different polymer cores or accessing unique stimuli-responsiveness through orthogonal non-covalent interactions. Supramolecular polymers have been demonstrated to assist in overcoming the inherent immiscibility of many blend compositions through their favorable non-covalent interactions.[134–136] The orthogonality of the assembled supramolecular networks can play an important role in dictating material behavior in blend formulations displaying different supramolecular binding chemistries. For example, it has been shown that UPy groups can competitively bind specific metals when blended with a metal-coordinating polymer; the interactions—or lack thereof—between networks offered stark changes in both material mechanics and stimuli-responsive behavior.[137] The opportunity to turn 'on' or 'off' supramolecular interactions between such blend networks through the presence of polymeric additives has also been explored, wherein a heterotelechelic supramolecular polymer was used to compatibilize orthogonal non-covalent assemblies of UPy and lateral staking benzene-1,3,5-tricarboxamide (BTA) polymers.[138] Via control of the orthogonality of supramolecular interactions, dynamic phase separation, which has been illustrated in dynamic covalent polymer networks,[139] can be explored as a potential avenue for modulating supramolecular behavior.

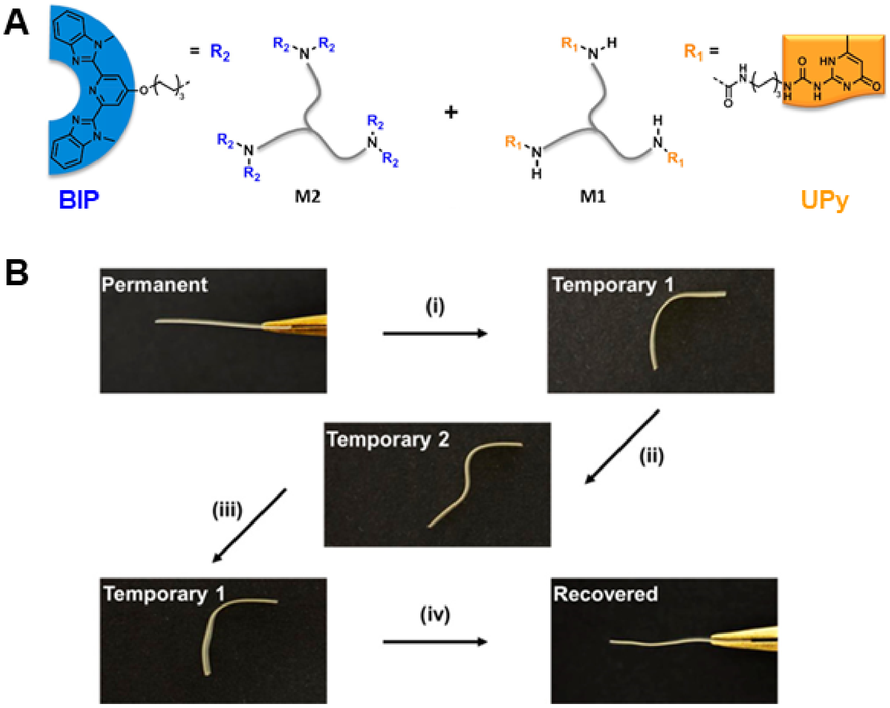

Figure 8: A) Structure of metal coordinated and hydrogen bonded blend components. B) Triple shape memory profile of supramolecular polymer blend. Films were (i) exposed to TMEDA vapors for 3 min, deformed, and dried under vacuum, (ii) heated at 110 ˚C, bent into an S-shape, and cooled to room temperature, (iii) reheated to 110 ˚C to recover the hydrogen bonding network shape, and finally (iv) re-exposed to competitive ligand TMEDA to recover permanent shape. Adapted with permission from ref. 133. Copyright 2019 American Chemical Society.

Crystallinity and supramolecular self-assembly. As with covalent crosslinks, the presence of crystalline regions in supramolecular polymers can be used to modulate self-assembly by adding another layer of interactions within the polymer chain. The organization of crystalline regimes has been shown to be widely sensitive to the presence of end groups and pendent functionality, which can hinder crystallization.[140,141] This behavior has been observed in telechelic supramolecular polymer systems, where the crystallinity of polyester cores decreased due to the reduction in segmental mobility caused by the association of supramolecular moieties.[78,142] The crystallization rate of the polymer backbone is also an important factor, where fast quenching of a molten supramolecular polymer can lead to a fully amorphous system due to competing organization of the supramolecular phase.[143,144]

While crystallinity and supramolecular self-assembly appear at first to have an antagonistic relationship, the specificity of supramolecular moieties can be used to achieve desirable crystal structures through strategic system design. One example of this approach is the stereocomplexation of UPy-functionalized poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) enantiomers. While it is well-known that the stereocomplex of these two enantiomeric polyesters displays a higher melting temperature when compared to the homopolymers,[145] the blending of high molecular weight PLLA and PDLA leads to a mixture of homochiral crystal and stereocomplex crystal structures, resulting in two distinct melting transitions.[146] By employing UPy at the chain ends of PDLA and PLLA, the formation of these stereocomplex crystalline regions can be accelerated and favored, resulting in materials with advantageous thermomechanical properties.[143,147,148] This enhancement in crystallization has been used to fabricate shape memory elastomers, where the formation of stereocomplexed crystalline domains could be used as semi-permanent crosslink junctions, while also allowing the thermally-labile UPy motifs to act as switching points for the fixing of a temporary shape.[147]

Nanofillers. In commodity polymer systems, modification of polymer properties also can be imparted by the addition of fillers, such as plasticizers or nanoparticles (NPs). In cases such as these, the presence of these fillers serves to modify thermomechanical, rheological, and electrical properties of the final material to meet application demands. Similarly, the precise use of these additives also can be extended to expand supramolecular polymer platforms. The inclusion of precise non-covalent interactions provides a pathway to modulate interactions with fillers through complementary or antagonistic supramolecular interactions, providing a mechanism to tailor material mechanics and stimuli-responsive behavior.

NPs and other nanofiller architectures have risen in popularity due to their tunability and potential for adding desirable stimuli-responsive behavior into a composite.[149,150] The dynamic behavior of supramolecular polymer systems offers functional handles to alter filler-matrix interactions. In some cases, the inherent surface chemistry of some fillers can be used to encourage compatibilization between the matrix and filler.[23,151–153] By relying on weaker but abundant interactions between carboxylic acid residues and Zn^{2+} metal centers, for instance, it was shown that favorable matrix-filler interactions could be introduced in a metal-coordinated BIP-based supramolecular nanocomposite containing cellulose nanocrystal (CNC) fillers as a means of increasing tensile stiffness.[154] However, these interactions may be detrimental in some cases; due to the competitive coordination of the CNCs, adjustment of the metal stoichiometry was required to obtain optimal self-healing and nanocomposite mechanics in the resultant films. In another example, direct supramolecular bonding between the matrix and filler has been shown to enhance compatibility and, as a result, increase stiffness and tensile strength;[155,156] however, nanofiller aggregation may occur if no preferential binding between the matrix and filler is introduced to compete with filler-filler supramolecular interactions.[151,152]

In some cases, the use of nanofillers can promote stimuli-responsive behavior of the supramolecular nanocomposite. For example, magnetic Fe_3O_4-based NPs decorated with UPy-functional polymers facilitated the construction of functional supramolecular nanocomposites.[157] The nanoparticles imparted both magneto-responsive behavior, although it was hindered by the decreased mobility associated with supramolecular self-assembly, and near-infrared (NIR) responsive shape memory and self-healing behavior due to the photothermal behavior inherent to

Fe_3O_4 NP systems. In another example, thermally-reduced graphene oxide (TRGO) was used as a nanofiller for supramolecular polymers constructed from diaminotriazine (DAT) and cyanuric acid (CA) attached in a pendent architecture to a poly(glycidol) core (**Figure 9A**).[158] As with the metallic Fe_3O_4 NPs, the TRGO displayed photothermal behavior in the NIR region. The local heat generated during irradiation promoted self-healing in the composites. Moreover, the spatial control offered by photo-driven stimuli-responsive processes allowed for film mechanics to be spatially controlled during deformation (**Figure 9B and C**). Controlled pulses of light could locally increase stress relaxation due to the enhanced rate of supramolecular bond exchange as local temperatures increased. Using digital image correlation (DIC), researchers tracked local displacement along a film under areal irradiation; due to the reversal of hydrogen bonding when the local temperature is increased, the irradiated areas showed increased local strain during tensile testing (**Figure 9C**).

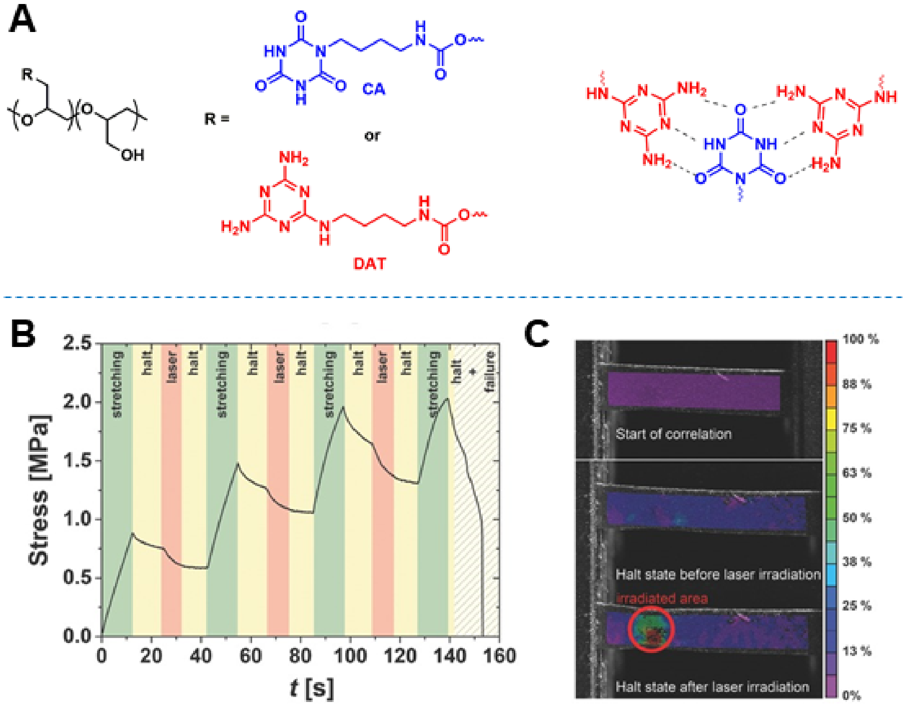

Figure 9: A) Design and self-assembly of hydrogen bonding supramolecular polymers based on a functional poly(glycerol). B) Spatially controlled relaxation experiments driven by a pulsed

NIR laser. Samples were stretched by 20% strain (green), held under tension for 10 s to equilibrate any initial relaxations (yellow), and irradiated for 20 s (red). C) DIC showing the increased local strain in areas of the film exposed to photoirradiation (circled in red). Adapted with permission from ref. 158. Copyright 2017 John Wiley & Sons

Aside from nanofillers, other additives, such as small molecules, can be used to alter the properties of supramolecular polymers. For example, the ultraviolet (UV) light absorber 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methyl-henol (Trade name: Tinuvin 326) has been used to effectively convert light to heat upon light absorption as a means of achieving reversible adhesion of hydrogen bonding supramolecular polymers.[23,159] This process facilitates the incorporation of photoresponsive behavior into the material without changing supramolecular chemistries or using nanofillers that require additional processing requirements, potentially leading to significant changes in material mechanics. In other cases, the inclusion of small molecules can be used to shift supramolecular polymer morphology or behavior. These small molecule additives can act as chain stoppers, which, when added to a telechelic supramolecular polymer, 'cap' the supramolecular chain end and limit the molecular weight.[160] In another example, Beyer *et al.* added small molecule BIP ligands to the corresponding pendent BIP-functional polymer to impact the morphology of the self-assembled system.[161,162] The addition of unbound BIP shifted the morphology from aggregates of the coordinated BIP to cylindrical assemblies. Additionally, the presence of the unbound BIP increased the concentration of the supramolecular hard phase, enhancing the storage modulus and creep resistance.

While the application of nanofillers into supramolecular polymer networks has been shown to reinforce dynamic polymer networks, interactions between the self-assembled matrix and the filler are critical for understanding how these materials behave. Nanofillers bearing self-complementary supramolecular interactions have encouraged matrix-filler interactions, but these fillers also can promote aggregation due to binding between supramolecular groups on the NP surface.[151,163] However, the use of 'neutral' NPs that don't interact with these dynamic handles could present other issues; it has been shown that network defects larger than the sizescale of the assembled supramolecular moieties could drive local dissociation of the assemblies; as such, the lack of interactions between the supramolecular polymer and filler could lead to a reduction in mechanics.[151,164] With this in mind, tuning NP surface chemistry to interact favorably with different aspects of the supramolecular motifs is key to optimizing NP dispersion without sacrificing the stability of the supramolecular arrays. This approach has been demonstrated by Jayaraman *et al*. using coarse-grained modeling to highlight that—when hydrogen bonding donors and acceptors are present exclusively on the polymer matrix and polymer-grafted NP, respectively—both the wetting between the matrix and NP and the NP dispersion are improved.[165] Moreover, extending the fillers to include small molecule additives is a promising avenue to tailor self-assembly without compromising the long-range assembly of the supramolecular network.

Supramolecular Polymer Processing and Device Fabrication

As our understanding of how self-assembly can be modulated *via* precision engineering of supramolecular polymers advances, the fields in which these supramolecular polymers can be applied also expands. Their inherent stimuli-responsiveness and modular mechanical toughness makes them prime candidates for the development of smart materials, where their tunable mechanics and stimuli-responsiveness can be used to design robust products such as wearable or tear-resistant devices and sensors. Tailored responses can be elicited through careful control over the organization of supramolecular polymers and how it interacts with other active components of the device.

In one approach, the supramolecular motif can be directly tied into the sensing functionality. By incorporating UPy and spiropyran into a PTHF prepolymer, Weng *et al*. designed a modular stress-sensing elastomer, where the increased toughness offered by the assembly of the supramolecular groups also served as a strategy for modifying the mechanoresponse of the spiropyran motif.[166] Alternatively, the supramolecular polymer can be used to support the constructed device. For example, Bao *et al.* used healable supramolecular polymers containing metal-ligand coordination sites to construct supramolecular organic field effect transistors (OFETs).[46,91] When chain-centered bipyridine-functionalized poly(dimethyl siloxane) (bpy-PDMS) was employed (**Figure 10A**), tough, healable dielectric elastomers were generated when the bipyridine groups were coordinated to Fe^{2+} or Zn^{2+} metal salts.[46] The supramolecular dielectric elastomers were fashioned into OFETs by layering them between an organic semi-conductor (OSC) and an EGaIn gate electrode on a silicon wafer (**Figure 10B**). The high polarizability of the metals increased the dielectric constant of the bpy-PDMS elastomers, offering a convenient avenue to reduce the operating voltage in the fabricated device. Interestingly, while using larger and more mobile counteranions such as ClO_4^- improved the healing efficiency of the bpy-PDMS, Cl^- anions led to less hysteresis when a voltage was applied. This behavior was attributed to the stronger coulombic forces binding the Cl^- groups to the metal salt preventing drift of the anion when the gate is open. Stretchable transistors, where a hydrogenated styrene-butadiene copolymer (SEBS) was used in place of the silicon wafer, boasted low hysteresis in transference curves even when stretched to 100% strain (**Figure 10C**); moreover, there was little gate leakage even after 1000 stretching cycles at 100% strain.

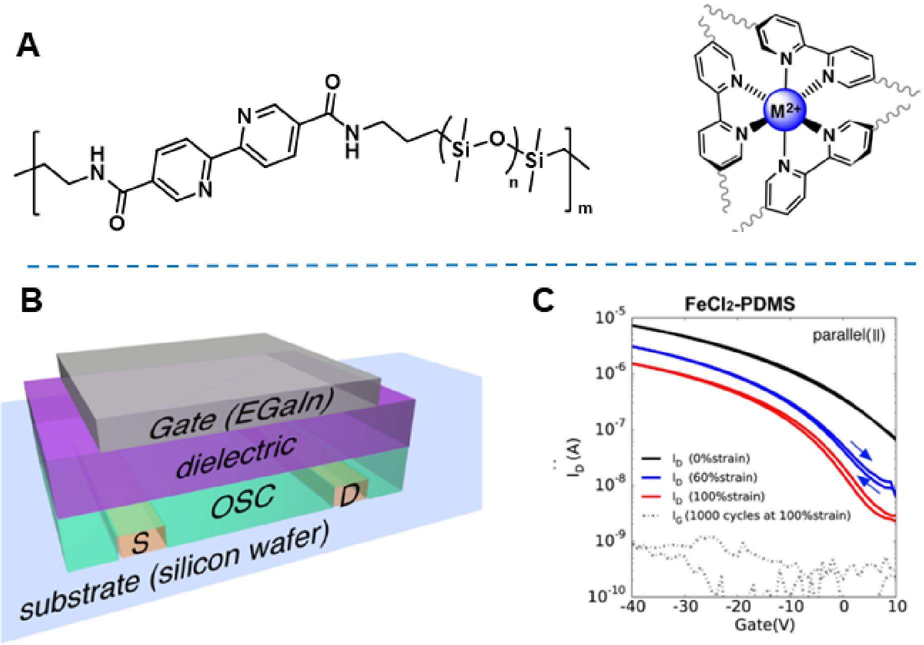

Figure 10: A) Structure of bpy-PDMS elastomer (left) and coordination geometry of bpy ligands to divalent metal centers (right). B) Schematic of OFET device fabricated on a silicon wafer with gold electrode (S and D) sandwiched under the OSC layer. C) Transference curves of bpy-PDMS-based OFET device containing $FeCl_2$ metal salts showing the low current hysteresis at multiple strains and the low gate leakage (I_G, dashed lines) of the device. Adapted with permission from ref. 46. Copyright 2016 American Chemical Society.

Supramolecular polymers are also attractive platforms for the development of tissue scaffolds due in part to their dynamic mechanical behavior, where recovery of stress after deformation can mimic that of natural tissues.[3] In many cases, these materials are processed, often utilizing electrospinning, into fiber constructs suitable for tissue engineering scaffolds.[3] The electrospun fibers exhibit enhanced surface area when compared to films, increased porosity allowing for cell and nutrient penetration, and can be spun in diameters in the range of tens of nanometers to tens of microns; moreover, these characteristics can be tuned to allow the electrospun fiber mat to better match the structure of the desired implant site.[167,168] Electrospinning of supramolecular polymers has been shown to be highly dependent on their interaction strength; Hayes *et al.* demonstrated that increasing the K_a of hydrogen bonding chain ends resulted in a transition from droplets to long fibers due to the increased effective molecular weight driven by the stronger hydrogen bonding interactions.[169] This processing approach has been utilized to fabricate scaffolds of UPy-telechelic poly(caprolactone) (PCL)-based materials, which exhibit minimal cytotoxicity and support the growth of new tissue.[92,170] Electrospun UPy-PCL scaffolds have been shown to exhibit different degradation behavior compared to conventional PCL fiber mats, where the oxidative sensitivity of the supramolecular fiber mats was modulated by changing the molecular weight of the polymer backbone to increase or decrease the concentration of supramolecular groups.[171] Moreover, the recognition inherent to supramolecular self-assembly has been utilized to produce bioactive supramolecular scaffolds containing UPy-functional peptides incorporated into the scaffolding matrix (**Figure 11A**).[172–174] The modified peptides were incorporated into the UPy hard phase without disrupting the organization of the supramolecular polymer; this strategy allowed for cell-signaling peptide sequences to enhance cell adhesion and differentiation without compromising the integrity of the non-covalent interactions. Dankers *et* al. used these bioactive supramolecular motifs to construct supramolecular renal membranes that assisted in the differentiation and function of human primary tubular epithelial cells (PTECs).[175–177] The employed UPy-telechelic polyester (PCLdi(U-UPy) (**Figure 11A**) exhibited a phase separated nanofiber morphology; when fabricated into micron-sized electrospun fiber mats, this supramolecular polyester mimicked the fibrous hierarchical structure of the extracellular matrix (ECM). These scaffolds were seeded with PTECs under static conditions and perfusion flow conditions, the latter of which closely mimicked the natural environment of the PTECs. Bioactive supramolecular scaffolds containing cell-signaling peptide sequences not only encouraged the growth of these renal cells into monolayers mimicking their natural structures (**Figure 11B**), but continued to support the growth and differentiation of PTECs during a nineteen day culture period.[176] These experiments demonstrate the biocompatibility of supramolecular groups as well as how these non-covalent interactions can be used to incorporate bioactive agents into the scaffold without harming the structural integrity of the scaffold.

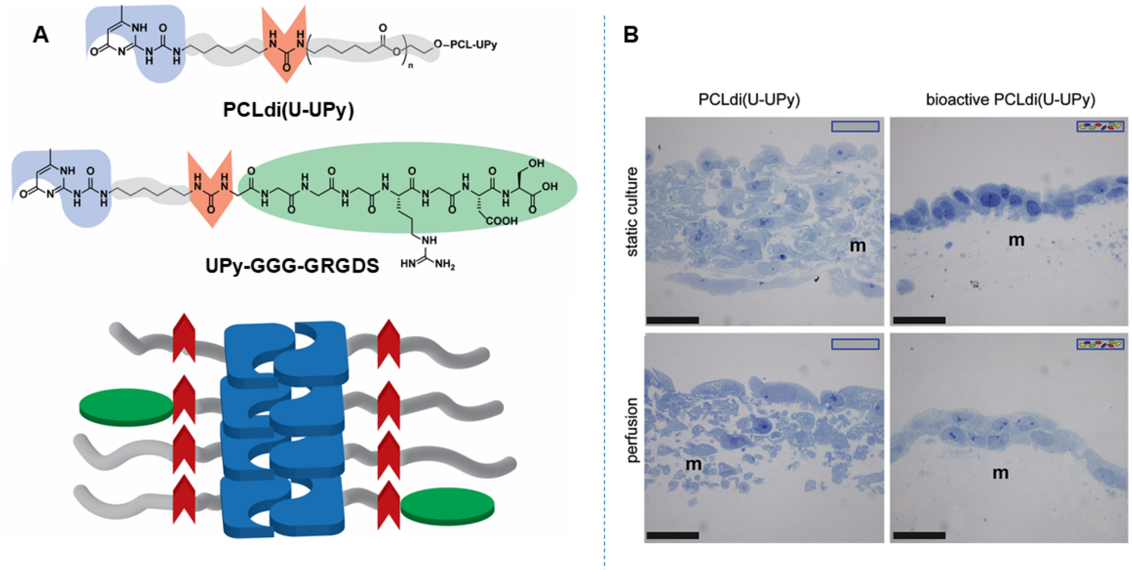

Figure 11: A) Structure of PCL-di(U-UPy) highlighting the UPy groups in blue and urea groups (U) in red. The bioactive supramolecualr peptide, UPy-GGG-GRGDS is depicted with the cell signaling agent highlighted in green. B) Toluidin blue stain of PCLdi(U-UPy) and bioactive PCLdi(U-UPy) highlighting the formation of monolayer membranes (labelled m) in the bioative scaffold. Adapted with permission from ref. 176. Copyright 2011 Elsevier.

Additive manufacturing offers opportunities to translate the dynamic nature of supramolecular interactions into complex macroscopic shapes and geometries while retaining the desirable stimuli-responsive functionality.[178] In some cases, supramolecular polymers can be used to reinforce commercial polymers in 3D printing processes. For example, the inclusion of only 1 wt% of a random copolymer of poly(methylmethacrylate)-*co*-(ureidopyrimidinone methacrylate) (PMMA-*co*-UPyMA) in a PMMA matrix increased the Young's modulus and tensile strength of materials produced *via* FDM printing.[179] Long *et al.* demonstrated the FDM printing of a chain-extended polyurea containing chain-centered, quadruple hydrogen bonding, cytosine derivatives (**Figure 12A**).[180] The supramolecular ordering within the hard domain of the polyurea offered enhanced mechanics through the physical crosslinks and microphase separation of the supramolecular assemblies, yielding prints with high extensibility and toughness both when the direction of stretch is parallel (0˚) or perpendicular (90˚) to the direction of printing; this mechanical response was attributed to increased adhesion between printed layers facilitated by this hydrogen bonding (**Figure 12B**). This strong hydrogen bonding landscape also contributed to the excellent printability, where complex shapes, such as the DNA double helix, could be produced without the need for structural supports (**Figure 12C**). Binder *et al.* used barbiturate-functionalized linear PIB and PEG in extrusion-based 3D printing to probe how phase separation contributed to print stability; while the barbiturate groups formed phase-separated micellar clusters when attached to the non-polar PIB, the increased polarity of PEG limited phase separation and led to substandard 3D prints.[181] However, when the 3-arm star barbiturate-functional PIB was added to the linear PIB (3:1 molar ratio of linear:3-arm star PIB) resulting in a miscible supramolecular polymer blend marked improvement in print stability was exhibited; whereas printed parts of linear supramolecular PIB displayed loss of their shape in 24 h due to creep and reorganization of supramolecular groups, the blends maintained their printed shapes even after 10 days. This behavior was driven by the increased number of crosslinking points incorporated due to blending of the 3-arm star PIB supramolecular material into the printing formulation. Hayes *et al.* demonstrated the printing of biocompatible PCL oligomers end-capped with functional urea derivatives using ink jet printing.[182] An important balance was struck between supramolecular interaction strength and printability, where benzyl-amine capped ureas showed better printing resolution than stronger hydrogen bonding UPy. In other examples, the incorporation of supramolecular groups into 3D printed materials provides a modular framework to design stimuli-responsive systems. UPy-functional monomers were copolymerized with PCL-dimethacrylate using digital light processing (DLP) to yield materials with self-healing and shape memory capabilities.[183,184]

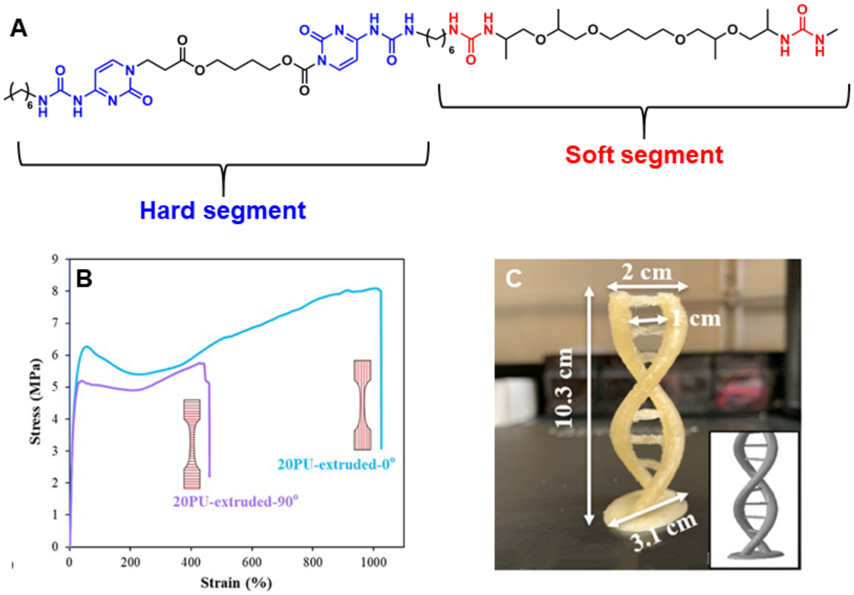

Figure 12: A) Structure of quadruple hydrogen bonding cytosine-derived polyurea. B) Tensile testing curves of prints stretched parallel (0°) to the direction of printing and perpendicular (90°) to the direction of printing. C) 3D printed DNA dobule helix. Inset: CAD file of the DNA double helix for comparison. Adapted with permission from ref. 180. Copyright 2020 American Chemical Society.

Conclusion and Outlook

Here, we highlighted advances in supramolecular chemistry and assembly as a pathway to tailor supramolecular interactions and organization to generate modular and responsive materials. There are vast amounts of binding motifs available, where the interaction type, assembly architecture, and polymer core identity all play pivotal roles in shaping the final material behavior. Beyond chemical strategies, control of supramolecular organization through modifications of polymer architecture or by the secondary characteristics of a polymeric material (*e.g.* crystallinity, covalent crosslinks) has proven to be a promising avenue for controlling responsive behavior in these materials. By selectively tuning interactions within the supramolecular phase or between matrix and filler, a wide array of responsive mechanics and thermal behavior are realized.

As the field of supramolecular self-assembly expands, more complex materials will be required to accommodate evolving technological needs. Some areas that have already benefited from concepts derived from supramolecular polymeric assembly aside from those discussed previously in detail, include organic light emitting diodes (OLEDs) and photovoltaic materials.[129,185,186] In such cases, the ability of supramolecules to form well-ordered nanostructures can be used to encourage sorting of molecular arrays, enhance toughness and tear resistance, and promote polymer blend miscibility can expand applications of these materials. Enhanced understanding of how the organization of these supramolecular arrays is dictated by their environment will facilitate innovation of these next generation materials. Toward enhanced behavior, the characterization of these hierarchical supramolecular polymer arrays is an important facet of the design of these materials.[187] In particular, advanced characterization techniques, such as X-ray or neutron scattering and rheology, are vital tools to probe important facets of the supramolecular system, such as organized nanostructures and relaxation behavior, respectively. For example, the applicability of time-temperature superposition (TTS) and the sticky-Rouse model have been examined for a series of pendent-functionalized supramolecular polymer melts using rheology.[111] Moreover, these dynamic studies can be extended to other polymer architectures, such as supramolecular brush polymers, to better understand how changes in polymer architecture play a role in governing dynamic self-assembly.[104]

Beyond the experimental approaches described here, simulations hold great promise as a powerful platform to understand and predict the organization and interactions in these complex systems.[165,188–190] In one example, molecular dynamics and Monte Carlo simulations were used to examine the growth of a physically crosslinked supramolecular network formed by telechelic supramolecular chains.[189] By changing the sticker binding energy, different equilibrium association behaviors could be simulated and snapshots of partner exchange as a dominant means of relaxation in the supramolecular material were observed. Computational strategies such as these offer unique snapshots into the formation of supramolecular networks in controlled environments, allowing researchers to gain important insight into how these systems may behave experimentally.

Since its widespread use in the field of macromolecular science and engineering, supramolecular interactions have greatly impacted the design and applications of responsive and dynamic polymeric systems. Here, we have presented examples of several research platforms that utilize self-assembly to unlock the full potential of supramolecular polymer systems by shifting the supramolecular chemistry, modifying aspects of the polymer backbone, and fabricating complex devices. Particular attention was given to how organization of supramolecular motifs can be modulated by shifting parameters, such as polymer crystallinity and covalent crosslinks. Continued growth in supramolecular polymeric systems will lie at the interface of chemistry, engineering, and physics due to the complex organizations and interactions driven by the inherent dynamics of the supramolecule.

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