

Non-covalent side-chain polymers: design principles, functionalization strategies, and perspectives

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Received 4th May 2004

First published as an Advance Article on the web 28th January 2005

DOI: 10.1039/b311285n

Side-chain functionalized polymers have a profound impact on complex materials synthesis with a variety of applications ranging from liquid crystalline and electro-optical materials to drug delivery systems. In the last decade, the use of self-assembly towards the synthesis of side-chain functionalized polymers has been investigated extensively as a result of its modular character and ease of synthesis. This *tutorial review* describes recent advances in the literature and establishes basic design principles and synthetic approaches towards the fabrication of supramolecular materials that are based on side-chain functionalized polymers.

1 Introduction

From before Linus Pauling's groundbreaking work on the hydrogen bond in the 1930's¹ to Jean Marie Lehn's 'Chemistry beyond the molecule' that led to the term 'supramolecular chemistry', the nature of non-covalent bonds has fascinated chemists for over a century.² In particular, the last thirty years have been exceptionally fruitful for scientists from a variety of disciplines who have made enormous advances in exploiting the non-covalent bond to construct sophisticated architectures.^{2,3} As macromolecular structures and functional materials have continued to evolve with higher degrees of complexity and function, traditional covalent-based synthetic strategies have become increasingly difficult to employ. Accordingly, many scientists have begun to replace traditional polymer synthesis with self-assembly in order to overcome a variety of

synthetic hurdles and to exploit the dynamic nature of the non-covalent bond.³ Tremendous growth and elegant advances in polymer science have taken place as supramolecular science, self-assembly, and polymer chemistry continue to converge.³ This review explores the design principles and functionalization strategies inherent to one class of supramolecular polymers, side-chain functionalized polymers (SCFPs), and will highlight the advances that have given rise to the sophisticated non-covalent functionalization methods of today.

1.1 Supramolecular polymers

Supramolecular polymers can be defined as 'the formation of polymeric materials *via* non-covalent interactions using self-assembly'.³ In biology, complexity and molecular function can be attributed to Nature's efficient use of non-covalent bonds to form advanced polymeric architectures such as DNA and proteins.⁴ Whereas in polymer science, functional materials are

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based mainly upon covalent bonds with limited accounts of self-assembly as a chief design motif. Nevertheless, self-assembly has become an important subfield of polymer science, arising as a consequence of major advances in the fields of molecular recognition and small molecule self-assembly.² Furthermore, progress in the field over the last decade has led to the development of general design principles that govern the synthesis of supramolecular polymers.^{3,5,6}

Supramolecular polymers are typically divided into two major categories, main-chain and side-chain.³ Main-chain supramolecular polymers can be described as polymeric systems that are held together by strong and directional non-covalent interactions in the polymer backbone or main-chain. In contrast, side-chain supramolecular polymers are based on a covalently linked polymer backbone that contains molecular recognition units on its side-chain and can be functionalized *via* self-assembly.

Over the past 20 years, main-chain self-assembled polymers have evolved greatly thanks to the pioneering work by Lehn and co-workers.² Today, a wealth of scientific research dedicated to the synthesis and study of main-chain polymers exists with examples of hydrogen-bonding and metal-coordination systems reported by a variety of groups.³ These accounts constitute the vast majority of literature reports on supramolecular chemistry with excellent reviews.^{2,3}

In comparison, self-assembled side-chain polymers have not yet attracted much interest despite the importance covalently based side-chain polymers hold for a variety of applications including drug delivery and electro-optical materials. Only a limited number of literature reports use self-assembly as a side-chain functionalization tool.^{7–40} Furthermore, no detailed review article describing the underlying design principles of supramolecular SCFPs is available. This report aims to close this gap by providing an account of recent and important progress in this exciting new field.

1.2 Basic design principles of side-chain functionalized supramolecular polymers

Before synthesis, the design of supramolecular SCFPs requires a number of choices to be made and requirements to be met that depend strongly on the nature of the polymer backbone as well as the desired application. In this section, we outline some important questions that should be addressed for the design of supramolecular SCFPs.

First, a decision has to be made whether the final polymeric material should be based on a self-functionalization or on a modular functionalization strategy. We define ‘self-functionalization’ as the functionalization *via* self-assembly of complementary recognition units along a single backbone (this can also be defined as intramolecular functionalization). Modular or intermolecular functionalization is the functionalization of a single polymer backbone *via* the non-covalent attachment of functional entities (Fig. 1). For example, the formation of hierarchical peptide architectures such as α -helices or β -sheets are based on self-functionalization while the replication of DNA is based on a modular functionalization strategy. In the second case the self-assembled small molecules are not covalently bound to the polymeric scaffold.

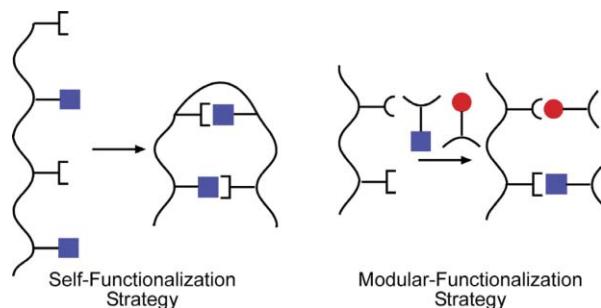


Fig. 1 Comparison between self- and modular-functionalization.

The second question that has to be addressed is when the desired functionalization should take place. Several scenarios are imaginable: i) the self-assembly step can precede the polymerization, ii) the monomer(s) containing terminal recognition units can be polymerized and subsequently functionalized, and iii) the recognition motifs covalently attached to the polymer backbone can be introduced in a post-polymerization step followed by self-assembly (Fig. 2). In all cases, only a limited number of polymerization methods may be successfully employed due to functional group incompatibility stemming from the recognition motifs.

Additionally, one must consider the number of recognition motifs contained within the polymer backbone (Fig. 3). Is only one type of side-chain functionalization needed for the desired application (single functionalization) or are multiple recognition units/events required (multiple functionalization)? Interestingly, all materials in Nature based on non-covalent interactions use multiple self-assembly motifs, whereas, the majority of synthetic systems employ only one self-assembly motif.^{7–25,31–40} This distinction clearly demonstrates a potential growth area for supramolecular SCFPs.

Fourth is the choice of the recognition motif(s) to be used. A large variety of recognition motifs and non-covalent forces have been reported for supramolecular polymers ranging from

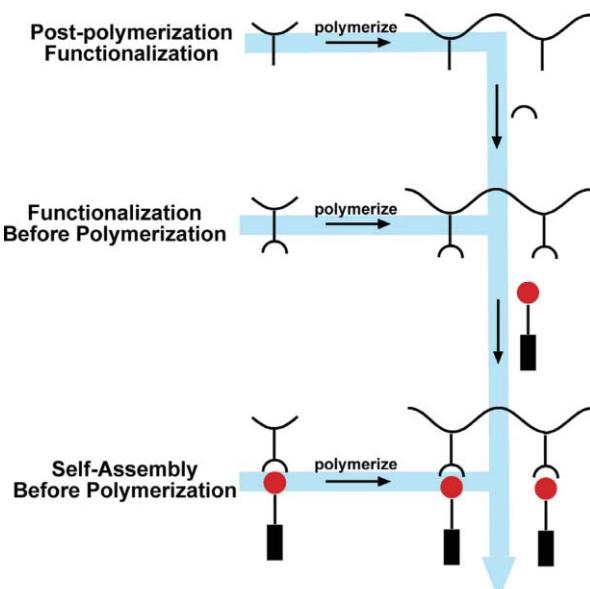


Fig. 2 Schematic display of various functionalization strategies.

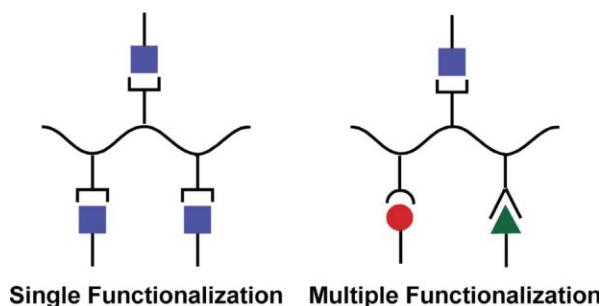


Fig. 3 Single-functionalization *versus* multi-functionalization.

π – π interactions and hydrogen bonding to metal coordination and electrostatic interactions.^{3,5,6,41,42} While in general these non-covalent interactions are categorized by the nature of the interaction such as hydrogen bonding or metal coordination, we will focus mainly on the resulting bond strength of the final self-assembled complex since this value will determine which interaction should be employed for a specific application. For example, polymeric materials for electro-optical applications have to be stable for thousands of working hours, thus requiring strong and stable non-covalent bonds. Whereas, systems designed for drug delivery require a weaker bond to facilitate drug release. Non-covalent interactions and forces can fall into three major classes: i) weak interactions ($0\text{--}15\text{ kcal mol}^{-1}$ bond strength), ii) medium interactions ($15\text{--}60\text{ kcal mol}^{-1}$ bond strength) and iii) strong interactions (above 60 kcal mol^{-1} bond strength). Due to their high dependence on external influences such as pressure, solvent, and temperature, most non-covalent forces do not fall into a single category. Fig. 4 describes the general division of non-covalent interactions based on bond strength. In general, single π – π , cation– π , hydrophobic, or van der Waals interactions or hydrogen bonds are very weak. In contrast some metal-coordination complexes (strongly dependent on the ligand system and the metal used) and electrostatic interactions have very strong bond strength. Multiple hydrogen bonds and some metal-coordination complexes can be categorized as medium strength.

Also the type of polymer backbone and polymerization method must be considered. Most reported systems employ a post-polymerization functionalization strategy to introduce the recognition unit.^{5,6,32} If a post-polymerization functionalization strategy is not employed, one must make use of polymerization methods that are functional group tolerant. Furthermore, if the formation of block copolymers is required or full control over molecular weight and polydispersity is desired, living polymerization methods must be employed. While a wide variety of polymerization methods are available



Fig. 4 Organization of non-covalent interactions by bond strength.

for the uncontrolled synthesis of supramolecular SCFPs, the choice of living polymerization methods is limited. The most common living polymerization method, living ionic polymerization, allows for full control during the polymerization but is intolerant towards many functional groups. Fortunately, other advanced techniques such as atom-transfer radical polymerization (ATRP), reverse addition fragmentation polymerizations (RAFT), or ring-opening metathesis polymerization (ROMP), tend to be highly functional group tolerant allowing easy access to well-defined architectures.^{43,44}

Last, the inherent reversibility of self-assembled polymers has to be considered. Depending on the non-covalent interaction, external influence such as temperature, phase (solid or liquid), solvent, pressure *etc.* will strongly influence the final polymeric structure. These external influences can be significant and most have been described extensively in the literature and will not be covered in this review.^{2,45}

Every consideration described above must be taken into account when designing supramolecular SCFPs. None of these issues is independent from each other. Examples in Nature are able to suggest important trends and tendencies, giving insight into the daunting task of combining these principles. However, natural systems have had billions of years to evolve. During the course of this review, we outline the evolution of this field highlighting important design principles employed thus far and suggesting potential areas for future advances.

2 Supramolecular side-chain functionalized polymers based on a single functionalization motif

Today, non-covalent functionalization strategies are largely based on a single recognition motif.^{5,6,35} Non-covalent grafting of molecular components to the side-chain of polymer backbones has been accomplished using a variety of non-covalent interactions.^{5,6,23,35} The most ubiquitous examples employ simple hydrogen bonds,^{5,6,45} with fewer examples that extend this methodology to ionic interactions, π – π stacking, or metal coordination.^{22–24} The earliest reported cases use a single non-covalent bond to attach a mesogen that is able to phase segregate to yield higher ordered architectures such as liquid crystalline phases.⁴⁶ Furthermore, many examples mimic Nature's ability to cooperatively bind a complementary recognition unit, citing the potential of these systems to mimic or interfere with biological systems. Other examples employ non-covalent cross linkers and hydrophobic or hydrophilic interactions to give rise to various micellar structures.²³ Regardless of the application, each of these systems relies on two types of design principles: 1) those that are specific to the intended application, and 2) those that can be generalized to all supramolecular SCFPs. The focus of this section is to highlight both aspects of this design strategy while placing an emphasis on general trends in functionalizing side-chain copolymers using a single molecular recognition motif.

2.1 Self-assembled side-chain liquid crystalline polymers (self-assembled SCLPs)

Non-covalent side-chain functionalization strategies were first reported for the synthesis of liquid crystalline materials.^{16,22}

Liquid crystals (LCs) possess orientational or weak positional ordering that give rise to materials with important characteristic of crystals but flow behaviour similar to liquids. Formation of this unique phase of matter is a direct consequence of the anisotropic alignment of small molecules or mesogens *via* non-covalent forces such as π - π stacking or hydrophobic interactions. Polymeric liquid crystals employ a variety of self-organizational processes to achieve long-range order. Conventional side-chain liquid crystalline polymers (SCLPs) are typically prepared *via* covalent tethering of mesogenic entities, structurally similar to low molecular weight LCs mesogens, with long, flexible aliphatic chains.⁵ This spacer group, situated between the polymer backbone and the mesogen, decouples the motion of the polymer from the side-chain giving flexibility to the molecular orientation of the mesogenic components. In the field of self-assembled SCLPs, the principles described above for SCLCPs are generally followed, yet covalent attachment of the mesogen is replaced with non-covalent bonds (Fig. 5).

Kato and Fréchet were the first to explore the non-covalent attachment of traditional liquid crystalline components to a variety of polymer backbones.¹⁶ In 1989 they disclosed their report describing binary mixtures of **2** and **3** to form thermotropic self-assembled SCLPs *via* simple single pyridine–benzoic acid hydrogen-bonded complexes (**1**) (Fig. 6).^{16,19} In this example, each component independently shows liquid crystalline behaviour. However, when 1:1 mixtures of **2** and **3** or **4** and **3** are prepared by slow evaporation from pyridine solutions, nematic mesophases with higher transition temperatures than those of the individual components are observed. This mesophase stabilization is attributed to the formation of extended mesogenic units involving the hydrogen-bond bonded complex **1** shown in Fig. 6.

While Kato and Fréchet's novel class of liquid crystalline polymers was based on a single weak non-covalent bond, this report held much significance not only for the field of self-assembled SCLPs, but also established fundamental design strategies for the preparation of supramolecular SCFPs in general. Following their original report, much effort was directed toward examining self-assembled SCLPs engineered with a variety of structural configurations.^{14,15,17,18,20} In particular, examples followed that included: i) the employment of anchored hydrogen-bonding complexes for the attachment of mesogenic components,^{15,18} ii) the self-assembly of two entities that individually show no liquid crystalline behaviour alone, but give rise to mesogenic hydrogen-bonded entities upon association,^{17,20} iii) the main-chain insertion of

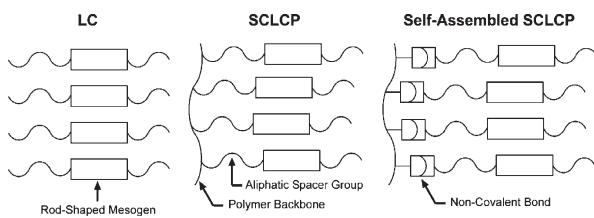


Fig. 5 Schematic illustration of the structural components used to fabricate simple LCs, SCLPs, to self-assembled SCLPs from rod-shaped mesogens.

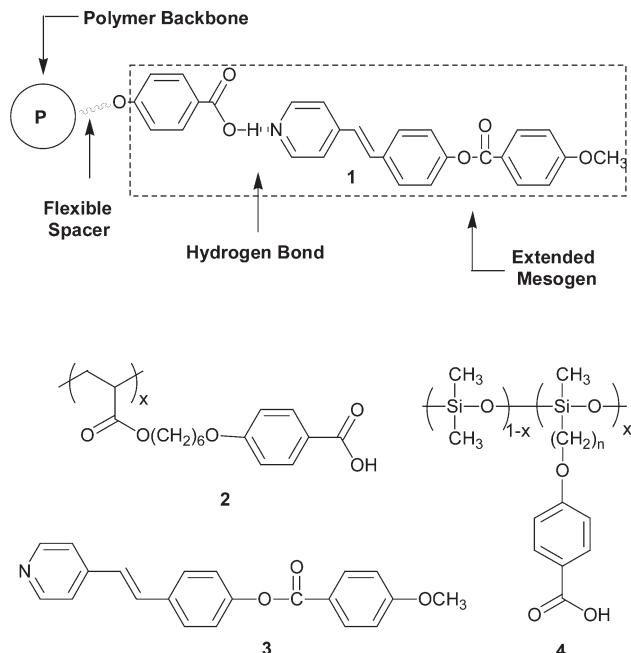


Fig. 6 Molecular components used to prepare the first examples of self-assembled SCLPs.

hydrogen-bonding units that can subsequently bind complementary hydrogen-bonding units that are tethered to a mesogenic component,¹⁴ and iv) the formation of liquid crystalline networks *via* the cross-linking of two polymer strands using bisfunctionalized hydrogen-bonding mesogenic entities (Fig. 7).^{18,36}

An important variation to Kato and Fréchet's original reports included the formation of self-assembled SCLPs where the hydrogen-bonding complexes do not form larger geometric objects specific towards an application but serve only as attachment points, molecular docking stations or anchoring

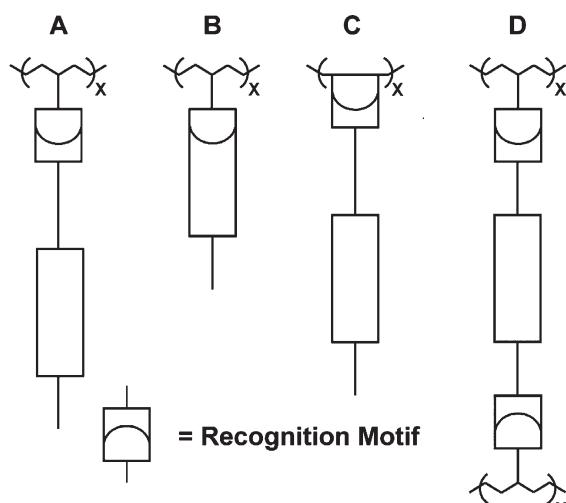


Fig. 7 Schematic illustration depicting a variety of structurally configured hydrogen bonded self-assembled SCLPs. A) Side-chain anchored mesogens, B) side-chain extended mesogens or mesogen formation, C) main-chain anchored mesogens, and D) cross-linked side-chain anchored mesogens.

groups, for functionalization (Fig. 8).^{15,18} In retrospect, this may seem to be a step backwards when compared to the enhanced stabilization gained from using extended mesogens or the elaborate approach of *in situ* mesogen formation. However, this methodology adds simplicity to self-assembled SCLPs by removing the difficult task of synthesizing complementary units capable of forming sophisticated architectures. Using this approach, any traditional LC mesogen or functional entity may be incorporated onto the side-chain, regardless of the resultant geometry of the self-assembled components (Fig. 7A). One example, that illustrates this concept, described the anchoring of conventional functional groups *via* covalent tethering of the well-known cyano-biphenyl mesogen to an imidazole-based hydrogen-bond acceptor.¹⁸ Subsequent self-assembly onto poly(acrylic acid) yielded hydrogen-bonded complex **5**, which gave rise to nematic liquid crystalline phase behaviour. The main advantage of this strategy is the potential for rapid optimization of liquid crystalline materials by eliminating extensive polymer and monomer synthesis. Many authors claim that by using this strategy the preparation of LC materials is reduced only to the synthesis of low molecular weight compounds possessing an anchoring unit and mesogenic components. Thus, rapid prototyping can be carried out *via* self-assembly.^{24,35} However, others contend that the procedures involved in preparing the individual components are just as cumbersome as the preparation of covalent SCLPs.²⁰ It is important to emphasize that the merits of both arguments hold true and each depend strongly upon two additional design factors: i) the methods used to obtain the polymeric scaffold and ii) the structural complexity of the non-covalent complexes.

In 1995, the groups of Mashelkar and Kato both reported the use of self-assembled SCLPs to create mesomorphic molecular assemblies that are based on two components, neither of which is liquid crystalline by themselves (Fig. 7B).^{17,20} The system reported by Kato and co-workers used doubly hydrogen bonded diaminopyridine-acid assemblies (**6**) to afford poly(acrylate)s possessing side-chain

mesogens formed as a result of self-assembly.¹⁷ This concept clearly extended the approach of liquid crystal mesogen formation *via* self-assembly introduced by Lehn and co-workers for main-chain liquid crystalline polymers in the early 1990s.⁴⁷ However, its scope is limited to the selection of complementary units capable of forming mesogenic entities through self-assembly.

Similarly, 2:1 mixtures of poly(acrylic acid) and bis-imidazoyl-terminated mesogenic compounds (**7**) gave liquid-crystalline network architectures *via* non-covalent cross-linkers using an anchored recognition motif (Figure 8).¹⁸ Even though analogous systems prepared with covalent cross-linkers do not show mesomorphism, these supramolecular polymers exhibited smectic A phases. This observation has been attributed to the dynamic nature of the hydrogen bond, which results in rapid exchange of the molecular pair, and thus suggests an explanation of the mesomorphic behaviour of the non-covalently bound system.

Perhaps, the most challenging aspects of synthesizing self-assembled SCLPs is the incorporation of the recognition motif into the monomer and the formation of the polymeric scaffold. The synthesis of polymers possessing recognition units must take into consideration a variety of factors including: i) the type of polymer backbone, ii) the physical and mechanical properties of the backbone, iii) the method used to incorporate the recognition motif, and iv) the polymerization technique to be employed. To illustrate this concept let us consider the benzoic acid functionalized self-assembled SCLPs first explored by Kato and Fréchet (Fig. 6). First, a decision to utilize a backbone amenable to the intended application was made based largely upon the desired physical properties of the resultant polymers and the ease of synthesis. Thus poly(acrylate)s and poly(siloxane)s were chosen. Secondly, a choice to either incorporate the benzoic acid moiety in the original monomer design or in a post-polymerization functionalization strategy required a detailed understanding of the polymerization technique. For example, poly(acrylate) **2** was obtained *via* free radical polymerization of 4-[(5-acryloylhexyl)oxy] benzoic acid (**8**) in DMF with AIBN.¹⁶ In this example, the polymerization technique is tolerant to the benzoic acid moiety and the synthetic challenges lie in the preparation of the monomer.

Although pre-functionalization may seem like a more elegant strategy, many polymerization techniques are often unavailable due to functional group incompatibilities. For example, **4** required modification of a prefabricated polymer backbone because poly(siloxane)s, prepared *via* condensation reactions, are functional group intolerant of carboxylic acids. Here, the benzoic acid moiety was introduced into the side-chain after the polymerization using a hydrosilation reaction with benzyl protected alkene **8** and commercially available poly(methylhydrosiloxane-co-dimethylsiloxane) **9** (Scheme 1).¹⁹ A second reaction, hydrogenolysis of the benzyl-protecting group, is required to yield the final polymer **4**. In this example, the synthesis of the polymeric scaffold was complicated by two post-polymerization reactions: 1) functionalization of the prefabricated polymer and 2) deprotection. Although successful, this strategy adds the stringent requirement that all reactions have to proceed in near quantitative

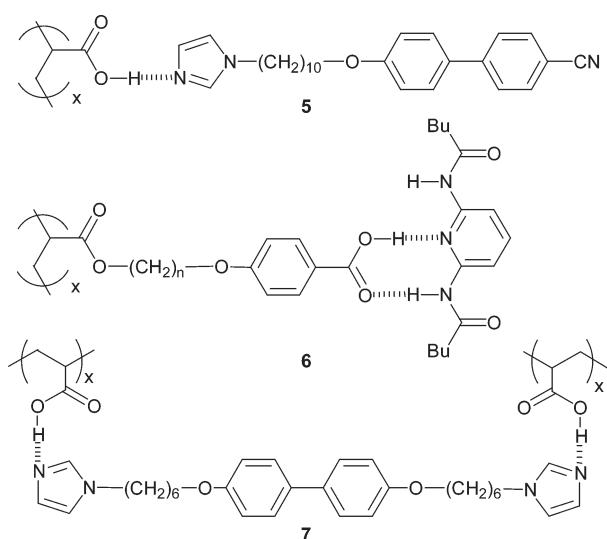
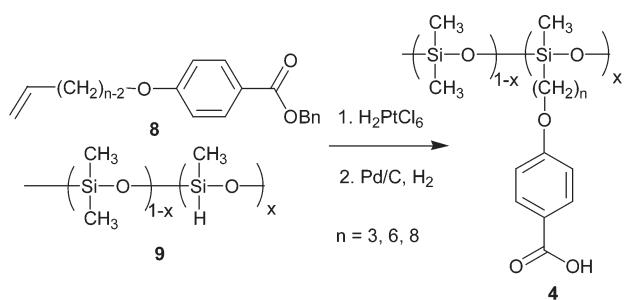


Fig. 8 Select examples of hydrogen-bonded side-chain liquid crystalline polymers.



Scheme 1 A post-functionalization route to polymeric scaffolds.

yields. Otherwise, incomplete reactions can lead to poorly defined systems limiting the utilization of self-assembled SCLPs in functional devices.

These early examples of liquid crystalline SCFPs are all based on very weak non-covalent interactions that contain either one or two hydrogen bonds. While these non-covalent interactions allow for dynamic bonding between the mesogens and the polymer backbones, the final self-assembled polymer properties are limited due to the inherent weakness of the hydrogen bonds. To overcome this hurdle, other non-covalent recognition motifs such as ionic interactions and metal coordination have been investigated following the basic design principles described above for hydrogen-bonding based systems.^{21,22}

Self-assembled SCLPs are the earliest and most widely studied class of supramolecular side-chain functionalized polymers. These studies clearly established a variety of design principles for supramolecular SCFPs in general and demonstrated that the concept of non-covalent side-chain functionalization can be used for the formation of an important class of materials. In recent years, literature reports have presented multiple iterations for optimizing the strength of the non-covalent interactions, the polymer backbone, as well as the liquid crystalline properties.⁵ At this time, no devices based on supramolecular side-chain functionalized liquid crystalline polymers have been reported, a drawback that should be addressed in the near future.

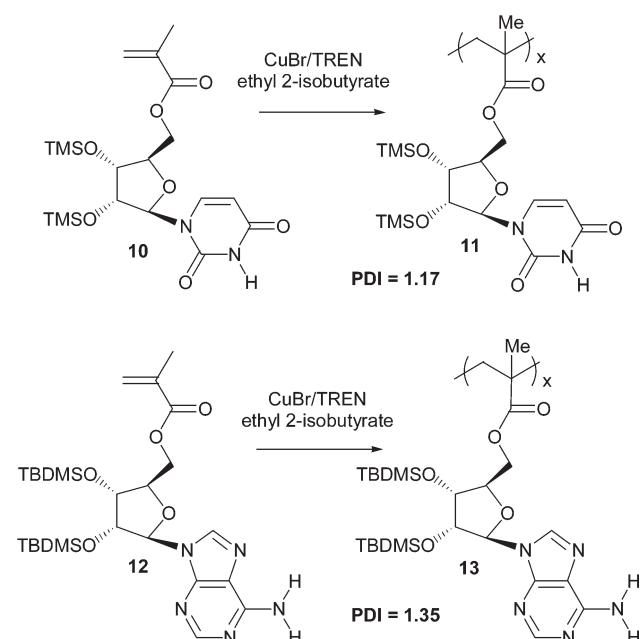
2.2 Nature inspired systems: advancements in the preparation and functionalization of hydrogen-bonding side-chain polymers

The best-known example of side-chain functionalization *via* self-assembly is DNA. The structure of DNA is rather simple, composed of only four complementary base pairs and a sugar phosphate backbone, yet it is arguably one of the most complex and dynamic functional biomaterials. It is well accepted that the diversity and intricacy of DNA is achieved primarily *via* Nature's efficient use of components capable of undergoing non-covalent interactions including hydrogen bonding.⁴ Decades after Watson and Crick reported the structure of DNA, many research programs continue to take design lessons from Nature, dedicated toward the preparation of side-chain polymers capable of imitating the complexity and functionality of DNA.^{7,9–11} These reports generally explore the synthesis of hydrogen-bonding polymers citing the high potential such systems hold for the preparation of advanced dynamic, reversible, and self-healing materials.⁴

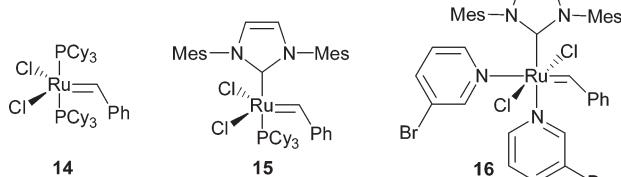
Fundamental to the exploration and exploitation of the remarkable structure–property relationships inherent to biopolymers is the synthesis of architectures that closely resemble those found in Nature. Research efforts towards this goal are hampered by the fact that most polymerization methods produce polymers with broad molecular weight distributions. In fact, most examples of bio-inspired polymers that incorporate molecular recognition units are synthesized either by using conventional free-radical polymerization techniques or *via* statistical attachment to poorly defined polymer backbones. These methods provide limited models of the monodisperse biopolymers found in Nature. Accordingly, much attention has recently been focused on the preparation of polymers *via* controlled polymerization methods such as ATRP or ROMP.^{19,43,44} These methods not only yield polymers with low polydispersities but also have high functional group tolerance and the ability to produce a variety of architectures including block copolymers.^{19,43,44}

For instance, Marsh and co-workers showed that ATRP could be employed to synthesize well-defined poly(nucleoside)-based polymers containing uridine and adenosine recognition motifs.¹¹ In this example, polymers **11** and **13** were synthesized with predictable molecular weights and low polydispersities (1.17–1.35). Additionally, these studies showed that ATRP is inert to many of the functional groups found in natural systems.

Perhaps the most robust polymerization method to date for preparing polymers with controlled architectures and low polydispersities is ROMP.⁴⁴ The early discovery that strained cyclic olefins could be polymerized in a living fashion with ruthenium-alkylidene catalysts has led to advances in the polymerization of functionally elaborate monomers.⁴⁴ Modification of Grubbs' ruthenium initiator **14** has led to the development of remarkably efficient and functional group tolerant catalysts (**15** and **16**).^{44,48}



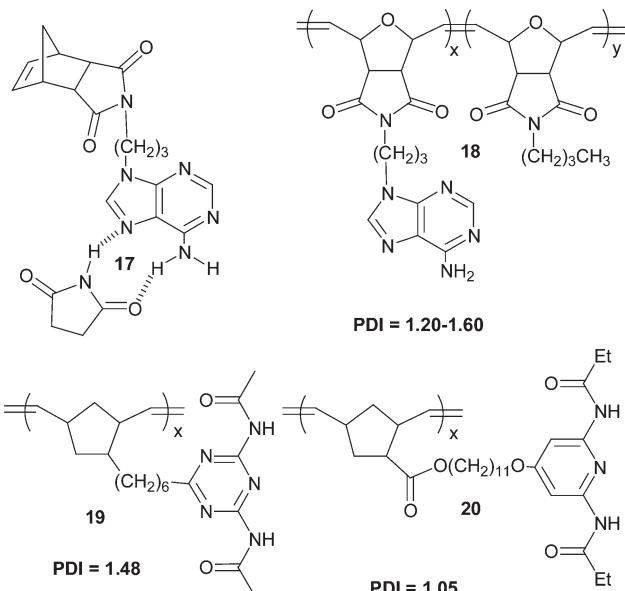
Scheme 2 ATRP of poly(nucleoside)-based monomers.



Gibson and co-workers first reported that thymine functionalized *exo*-norbornenes could be polymerized in a controlled manner (PDI = 1.07).⁹ However extension of this methodology to a variety of other nucleic-acid base containing monomers was hampered by low reactivity.⁸ Weck and co-workers developed new strategies to circumvent the poor polymerization of sluggish monomers. One strategy is based on the use of complementary molecular recognition units that serve as protecting groups during the polymerization that can be removed easily afterwards.¹³ They demonstrated this methodology in the synthesis of triazine-containing norbornenes *via* ROMP that have three hydrogen bonds per repeating unit accessible for side-chain functionalization. The second strategy is based on the removal of the carbonyl moiety from the vicinity of the ruthenium centre.¹³ Using this strategy, triazine or diaminopyridine-based moieties could be polymerized in a living fashion resulting in the formation of well-defined hydrogen-bonding scaffolds (**19** and **20**) that could be functionalized efficiently *via* self-assembly of small molecules containing complementary recognition units.^{12,13} Sleiman and co-workers reported the employment of the more active catalyst **15** for the homo-polymerization of adenine containing polymers, which showed improved conversion, but the resultant polymers only partially propagated due to poor solubility.⁷ To circumvent this limitation, they adapted the ‘protecting group strategy’ described above and polymerized adenine functionalized monomer **17** in the presence of a complementary recognition unit, succinimide, thereby eliminating competitive dimerizations.⁷ This methodology was then extended to the preparation of AB block copolymers (**18**) by sequential addition of adenine-functionalized norbornene:succinimide complexes to fully propagated, but non-terminated *n*-butyl functionalized poly(norbornene). However, this approach led to poorly defined copolymers because catalyst **15** gives rise to significantly faster rates of propagation compared to initiation, which leaves uninitiated **15** present upon addition of the co-monomer. Consequently, block formation must also compete with homopolymer formation upon addition of the second monomer.

These examples demonstrate the importance of the polymerization methods in the preparation of supramolecular SCFPs. For flexibility and control over the polymerization step, future systems will most likely employ fully functional group tolerant polymerization methods.

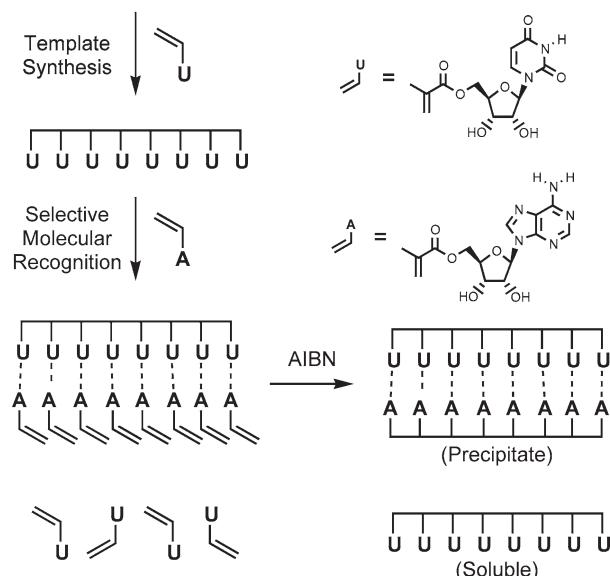
In addition to using controlled polymerization techniques to synthesize well-defined polymeric architectures, the use of template-directed polymerizations have been reported.¹⁰ Here, a prefabricated template structure selectively binds to functional monomers. Subsequent polymerization routes such as free radical polymerization (Scheme 4) yields a daughter



Scheme 3 Select examples of ROMP monomers and polymers containing grafted hydrogen-bonding units.

polymer possessing the exact structural features as the template with the exception that the resulting polymer possesses the complementary recognition units. Finally, the binary polymer assembly is precipitated and the two recognition units are separated.

Marsh and co-workers reported an example of this procedure.¹⁰ A template was prepared using free radical polymerization of uridine containing monomers. Subsequently, a mixture of adenine and uridine nucleosides was added to a solution of the template. Selective binding of the adenine nucleosides followed by exposure to a free radical initiator (AIBN) resulted in the formation of a poly(5'-acryloyluridine)-poly(5'-acryloyladenine) complex, which could be



Scheme 4 Template-directed polymerization.

selectively precipitated. Separation of the binary complex was achieved by selective dissolution of poly(5'-acryloyadenosine) in 0.5 M sodium hydroxide solution. Subsequent filtration of the remaining solid gave a 94:6 ratio of adenosine to uridine, indicating that the template process takes place with high fidelity of transcription from parent to daughter polymer.

Although the template method suggests an elegant route to highly regular and potentially monodisperse polymer structures, it suffers from several potential limitations. First, the structure of the final polymer is completely dependent upon the architecture of the parent polymer and is therefore limited to advanced polymerization strategies. Second, the separation procedures are not always quantitative and often extensive, leaving complementary residues in the samples. Third, weak non-covalent interactions will not be able to translate the parent polymeric scaffold quantitatively due to low association constant resulting in an imperfect self-assembly. Nevertheless, this method does show outstanding promise for functional group intolerant monomers that can be formed by no other means and for strong but reversible non-covalent interactions. For example, employing this methodology using a succinimide parent template initially created *via* “living” ROPM could potentially alleviate the problems associated with triazine polymerization described earlier.

Although the synthesis of well-defined polymeric architectures is often difficult, functionalization *via* self-assembly provides efficient routes, unmatched in their simplicity, to a variety of complex materials. Self-assembly allows one to easily modify the polymer structure, giving access to a multitude of functionalized polymers stemming from a single backbone. Rotello and co-workers have named this important class of scaffolds “plug and play” polymers for their ease of functionalization.³⁵ The dynamic nature of the non-covalent bond allows for control of intermolecular complexation in these systems *via* external factors such as solvent polarity and temperature. Fig. 9 depicts two potential ways one may functionalize “plug and play” polymers containing a single recognition motif. First, monofunctionalization can take place by mixing the scaffold with a functional entity anchored to the complementary unit. Second, multifunctionalization may be carried out by the addition of mixtures of one or more anchored entities to the complementary unit resulting in uncontrolled random multifunctionalization. This route has exceptional potential for the rapid optimization of novel materials based on compositional blends of functional components.

Kato has reported the first example of single recognition motif multifunctionalization for the preparation of SCLPs

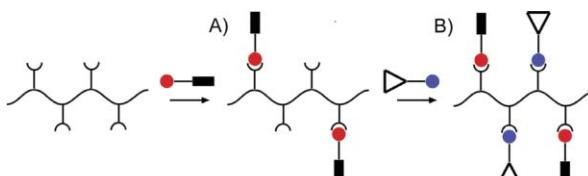


Fig. 9 Schematic depiction of single recognition motif “plug and play” polymer modification approaches: a) monofunctionalization and b) multifunctionalization.

from a blend of mesogenic components.^{36,37} Poly(acrylate)s possessing pendant benzoic acid moieties were added to binary mixtures of stilbazoles containing either electron donor ($-OCH_3$) or electron acceptor ($-CN$, $-NO_2$) end groups resulting in the formation of self-assembled multifunctionalized side-chain polymers (**22** and **23**). This methodology has also been extended to the formation of mesogenic three-dimensional networks *via* multifunctionalization using mixtures that incorporate both, bipyridine cross-linker **24** and stilbazole **25** (Fig. 10).

Rotello and co-workers have provided the vast majority of reports demonstrating the versatility of single recognition monofunctionalization in polymer science.^{31–35,40} This group's early accounts describe the design of poly(styrene)-based random copolymer systems, post-functionalized with donor-acceptor–donor hydrogen-bonding units.³⁵ In particular they studied the self-assembly of flavin (**28**) onto polymeric scaffolds (Fig. 11). Moreover, they showed that the efficiency of molecular association is directly related to the propensity of the pendant hydrogen-bonding unit to undergo intermolecular self-assembly. Polymers containing self-dimerizing triazine units were less effective in binding **28** ($K_a = 36\text{ M}^{-1}$) than closely related polymeric scaffolds based on diaminopyridine ($K_a = 220\text{ M}^{-1}$) because of the intramolecular association of triazines.³⁵

Rotello later reported an application of this methodology to the synthesis of hybrid materials.³² Here, polyhedral oligomeric silsesquioxane (POSS), a common inorganic additive in many nanocomposite materials, was tethered to a diaminopyridine (DAP)-based hydrogen-bonding motif. Non-covalent functionalization of random co-poly(styrene)s bearing thymine recognition units was accomplished *via* simple mixing of POSS–DAP in chloroform followed by slow evaporation of the solvent. The coupling of hydrogen-bonding directed self-assembly and POSS–POSS crystallization afforded the

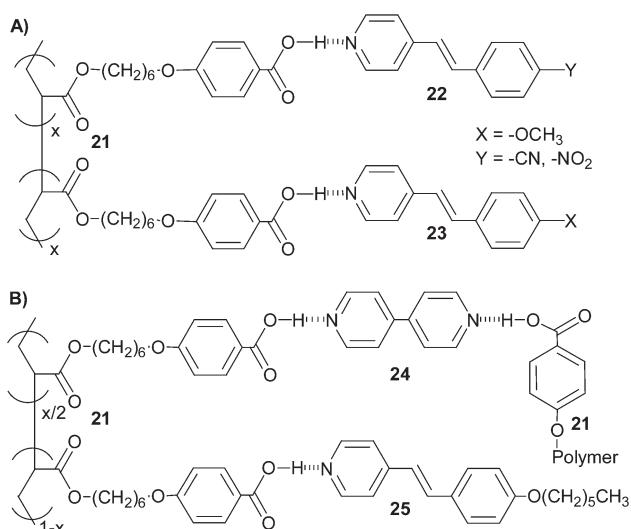


Fig. 10 Non-covalent attachment of mesogenic components *via* multifunctionalization strategies: A) blends of electron donor and acceptor mesogens and B) blends of cross-linker and stilbazole mesogens.

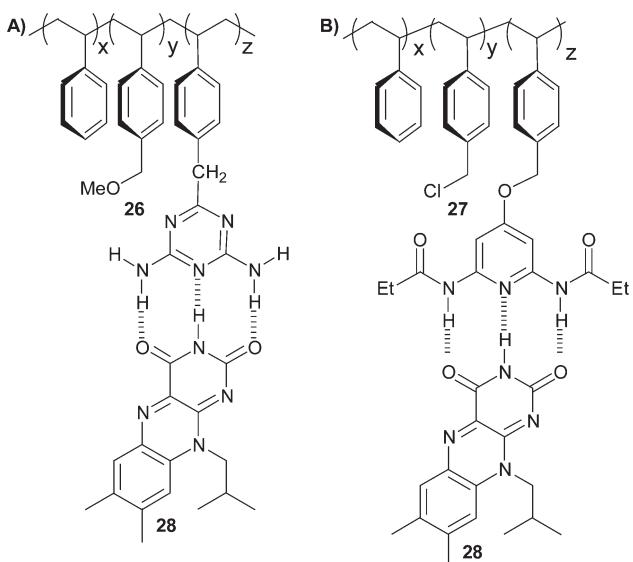


Fig. 11 Self-assembled complexes formed *via* intermolecular hydrogen bonding of a) a flavin **28** and diaminotriazine random copolymer **26** and b) **28** and diaminopyridine random copolymer **27**.

desired POSS/copolymer nanocomposite material rapidly and efficiently.

In another example of an application, Rotello and co-workers used self-assembly to control multi-scale ordering of spherical aggregates.³⁴ Gold nanoparticles possessing thymine residues were self-assembled onto block co-poly(styrene)s functionalized with the triazine moiety *via* hydrogen bonding. These systems were called “bricks and mortar” polymer-mediated self-assemblies.³¹ The use of diblock copolymers gives rise to microphase separation of the copolymer and the nanoparticles, allowing for control of the spherical aggregate size by simple modification of the poly(styrene) block bearing the triazine residue.

Building upon earlier examples describing the formation of recognition-induced polymersomes *via* polymer–polymer hydrogen bonding, a recent report by the Rotello group

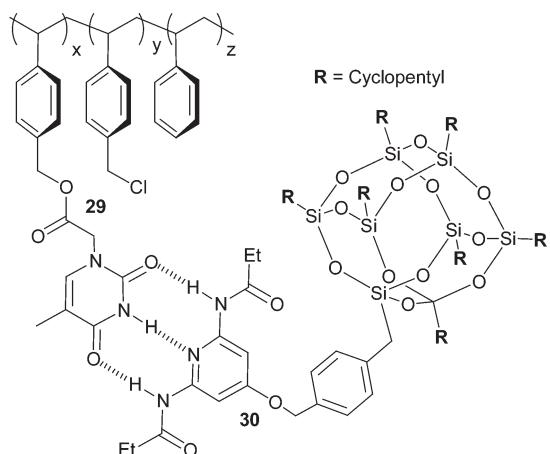


Fig. 12 Intermolecular complexation of thymine functionalized random copolymer **29** and diaminopyridine-polyhedral oligomeric silsesquioxane entities.

describes the non-covalent cross-linking of diaminopyridine functionalized copolymer **27** by the simple addition of a bis-thymine in a non-competitive solvent resulting in the formation of micron-sized aggregates (Fig. 13B).⁴⁰ Microsphere formation was thermally reversible with full destruction of the hydrogen bonds at 50 °C and subsequent reconstruction upon cooling to room temperature. In fact, the particle dispersities could be tailored through this basic annealing process demonstrating the ability of dynamic and reversible non-covalent systems to undergo self-optimization.

Ikkala and co-workers reported an excellent account of applying side-chain self-assembly to materials design.³⁹ Hydrogen bonded complexes composed of a 1:1 mixture of poly(4-vinylpyridine) and a non-mesogenic 3-pentadecylphenol surfactant were prepared, giving rise to lamellar secondary structures (**34**) (Fig. 14). Simple modifications of the surfactant to polymer ratios resulted in partial complexation and an observed increase in the long period.

By applying the same design principles to poly(styrene)-block-poly(4-vinylpyridine) block copolymers of appropriate block lengths, a lamellar substructure within a cylindrical mesomorphic architecture was formed (**35**).³⁸ The cylinders, formed *via* self-organization of hydrogen-bonded pentadecyl phenol were ‘emptied’ by washing away hydrogen-bonded surfactants exploiting the reversible nature of the non-covalent bond. Following the facile removal of the surfactant, the cylindrical structures remain in the rigid glassy poly(styrene) matrix. Since the pyridine-containing portion of the block copolymer is intact following surfactant removal, the inner walls of the cylinder can be described as “hairy tubes” or a mesoporous material containing hollow cylinders with polymer brushes lining the inner walls (Scheme 5).

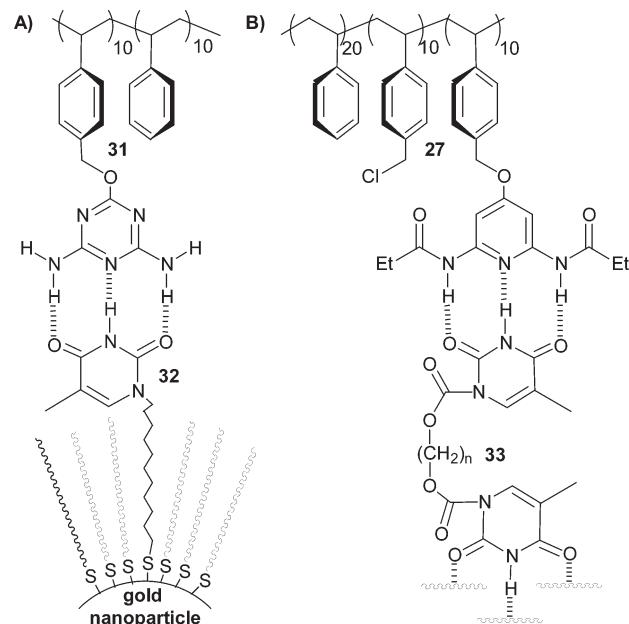


Fig. 13 A) Block co-poly(styrene)s containing triazine and diaminopyridine recognition motifs non-covalently attached to gold nanoparticles **32** and B) cross-linked with butylthymine **33** respectively.

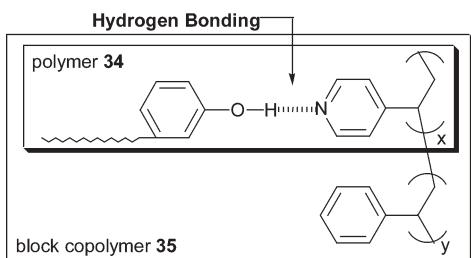
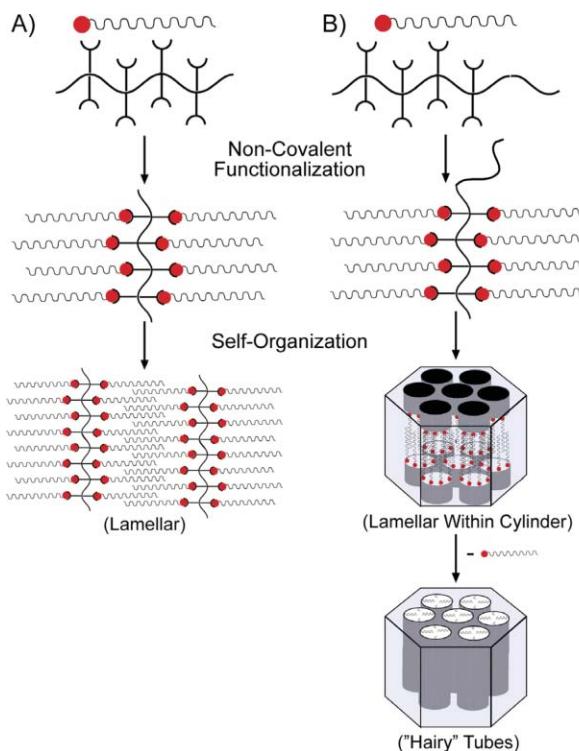


Fig. 14 Poly(4-vinylpyridine)-pentadecylphenol and poly(styrene)-block-poly(4-vinylpyridine) pentadecylphenol surfactant complexes used by Ikkala and co-workers.



Scheme 5 Hierarchical self-organization of side-chain self-assembled polymers. A) Systems stemming from the association between poly(4-vinylpyridine) and pentadecyl phenol and B) structures arising from the association between poly(styrene)-block-poly(4-vinylpyridine) and pentadecyl phenol.

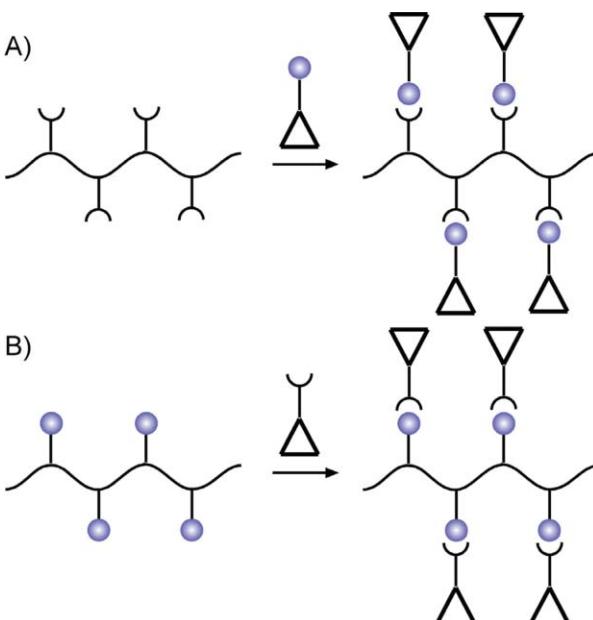
2.3 Side-chain metal containing polymers (SCMPs): engineered metal–ligand interactions, functionalization strategies, and applications

Side-chain metal containing polymers (SCMPs) belong to a unique sub-field of polymer science mainly concerned with the fabrication of novel catalytic and electro-optical materials. Here, the physical properties of both the inorganic and the polymer components exist simultaneously, giving rise to a variety of hybrid materials exhibiting metal-specific properties such as conductivity and magnetism while maintaining the benefit of solubility and processability inherent to the polymer backbone. Furthermore, SCMPs have been exploited as recyclable, homo- and heterogeneous transition metal supported catalysts and have been suggested for numerous other

applications including wastewater treatment additives, metal scavengers, liquid crystals, and NLO materials.⁴²

Although many examples of side-chain metal coordinated polymers exist, only a handful are designed to serve as recognition motifs for side-chain functionalization.^{23–25} These polymers represent a new class of metallo- “plug and play” materials that are similar in concept to the hydrogen-bonding systems described earlier, yet differ greatly because of the high bond strength of the interaction as well as the unique physical properties of transition metal complexes. In this section, we will review, outline, and discuss the important design principles, functionalization strategies, applications, and limitations of non-covalent side-chain functionalizations using metal coordination.

SCMPs fall into two classes according to the position of the metal complex with respect to the polymer backbone. In the first class, the metal is covalently tethered to the assembling building block, whereas the complementary component, a pendant ligand, is located along the side-chain of the polymer backbone (A). These scaffolds are sometimes referred to as polymeric ligands.⁴² The second class is based on a polymer–metal complex that is grafted onto the polymer side-chains and the desired functionalization step takes place *via* the coordination of a ligand based anchoring unit (B). In both cases, the resultant polymers may possess identical structures and the choice of the synthetic strategy is dependent on the ease of the synthetic method.



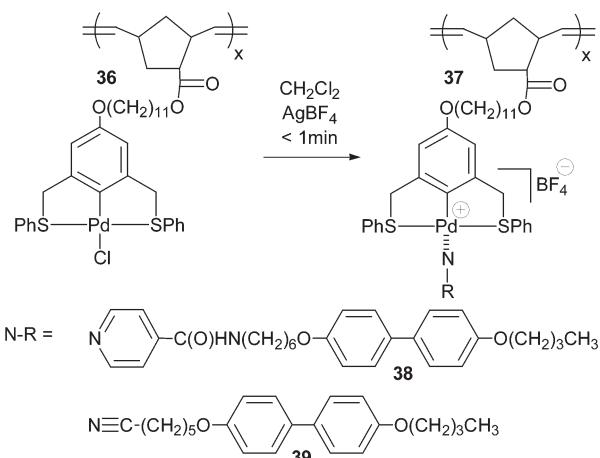
Therefore, the design of “plug and play” systems based on metal coordination requires careful attention in choosing between a polymeric ligand scaffold and a metal-containing backbone. Polymeric ligand-based scaffolds are generally easier to synthesize but less economical because of the required extensive synthesis of the metal-recognition motifs for each self-assembling component. However, the polymerization strategies available for these systems are numerous and usually straightforward. In contrast, the incorporation of a metal-complex into the polymer backbone is more economical due to

the ease of preparing an assortment of ligand anchored functional components, but is limited to a small number of polymerization methods as a result of the metal intolerance of most polymerization techniques. Although limited, accounts of mild polymerization strategies such as ROMP have been employed to prepare polymers possessing pendant metal complexes.^{12,24}

Weck and co-workers reported the preparation of poly(norbornene)s bearing palladated SCS pincer complexes (**36** and **37**) at every repeat unit using ROMP.^{12,24} These polymers were shown to polymerize in a living manner, which gave rise to low polydispersites and stoichiometric control over the molecular weight. In this example, the versatility of the “plug and play” methodology in metal-coordination systems was established by rapid and quantitative functionalization of **37** by using palladium–ligand interactions with a series of biphenyl-based mesogens (**38** and **39**) tethered to either nitrile or pyridine anchoring ligands.²⁴ The strength of the metal to ligand interactions was probed using thermal gravimetric analysis and showed that pyridine-anchoring units were thermally more robust than the nitriles. This led to a unique circumstance in which the self-assembled polymer could be easily altered by cleavage of the Pd–NC interactions *via* simple 1:1 mixing, and subsequent ligand displacement with a pyridine-anchored functional group. This ligand exchange exemplifies the ease with which polymers based on metal coordination can be modified, thus extending the concept of reversibility beyond the thermally labile hydrogen-bonded based systems.

Another system containing ligands in the backbone that has been reported includes terpyridine modified methacrylates that were copolymerized in the presence of methylmethacrylate using free radical polymerization methods (**40**).²³ In this example, **40** was functionalized with different terpyridine–ruthenium(III) trichlorides (**41**) in the presence of ammonium hexafluorophosphate and *N*-ethylmorpholine.²³ In the case of the heteroleptic bisterpyridine ruthenium(II) poly(ethyleneglycol) complex, aqueous micellar structures could be prepared.²³

The employment of metal-coordination units as recognition motifs gives rise to limitations not seen in hydrogen-bonding



Scheme 6 Metalloc-“plug and play” polymers with metal-coordination units positioned in the backbone.

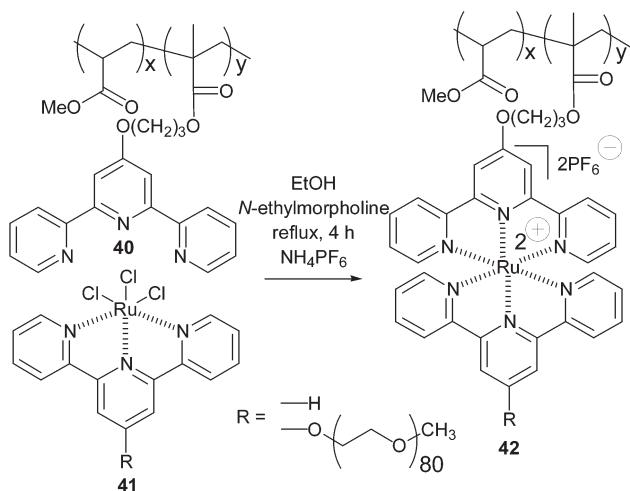


Fig. 15 Metalloc-“plug and play” polymers with terpyridine ligands.

motifs. First, the self-assembly step usually results in charge formation at each repeat unit often limiting solubility in organic solvents. However, this problem can be overcome by the attachment of solubilizing groups such as the alkyl spacer situated between the polymer and the recognition unit or by adding multiple alkyl chains to the ligand sphere of the metal complexes. However, this will further complicate the employment of such systems by increasing synthetic time. Second, the high strength of these non-covalent complexes is inferior to the dynamic nature of the hydrogen bond. Here, reversibility usually has to take place chemically *via* ligand displacement reactions. Only limited accounts of thermal reversibility exist. Schubert and co-workers showed that thermal bleaching could be observed for iron–terpyridine complexes at 210 °C.⁴¹ However this is an exception rather than the rule since transition metal complexes usually decompose prior to showing reversibility.⁴² Another limitation of metal-coordination based supramolecular polymer systems is the potential for complication during the characterization. Paramagnetic metal species cannot be easily analyzed *via* NMR while gel-permeation chromatography of SCMPs often fails due to aggregate formation of charges or shear induced rupture of the metal complexes.⁴² Despite these limitations, the field of SCMPs offers many opportunities to optimize organic/metal hybrid material properties as a result of the strong non-covalent bonds involved. As this area of supramolecular SCFPs continues to mature, exciting applications and novel solutions to these problems will inevitably emerge.

3 Supramolecular side-chain functionalized polymers based on multiple functionalization motifs

The main reason for research in supramolecular polymers is its simplicity and direct analogy to biological materials design, which uses extensively the concepts of self-assembly and non-covalent synthesis. However, in contrast to biological systems that use a wide variety of non-covalent interactions such as hydrogen bonding, metal coordination, and hydrophobic interactions in an orthogonal fashion to introduce function, diversity, and complexity, most supramolecular polymers are

based solely on one molecular recognition motif. As materials and polymer science continues to evolve, a movement toward polymers with increasing architectural complexity will be required. For example, many electro-optical materials based on side-chain copolymers rely on a fusion of multiple molecular components to form functional devices. State-of-the-art preparation of such materials requires copolymerization of monomers containing a large number of different components. In the future, supramolecular SCFPs for such applications will require multiple non-covalent interactions in order to meet the technological needs of tomorrow. Such systems will open new possibilities for the preparation of dynamic and rapidly optimized “smart” materials.

At present, all examples of supramolecular side-chain functionalized polymers based on multiple functionalization motifs fall into three categories: 1) systems where multi-functionalization using two or more non-covalent interactions join at a single anchoring site embedded along a polymer backbone (Fig. 16A),^{28–30} 2) systems with polymer backbones that contain two or more sets of recognition motifs, each one complimenting the other, allowing for self-functionalization or intramolecular folding to take place (Fig. 16B),²⁶ and 3) systems containing two or more discrete recognition motifs located along a polymer backbone that can bind their respective complementary recognition units selectively and intermolecularly, allowing for modular functionalization strategies (Fig. 16C).

Ikalla and co-workers have employed multiple interactions to fabricate supramolecular nanostructures with microstructural control on two different length scales.^{28,30} Here, more than one type of non-covalent bond is joined at a single anchoring site, thereby allowing for multi-functionalization at each repeat unit. The motivation for forming such complexes lies mainly in the ease of synthesis, allowing one to rapidly tailor the properties of the resultant materials. In one example, poly(4-vinylpyridine) was functionalized *via* proton transfer using methane sulfonic acid.²⁸ Subsequent mixing of the polymeric salt and pentadecyl phenol led to hydrogen bond formation between the phenolic hydroxyl group and the sulfonate group of methane sulfonic acid to provide polymers **43** and **44**. Microphase-separated diblock copolymer **44** self-organized to form structures-in-structures similar to those in Scheme 5 whose hierarchical phase transitions could be controlled systematically leading to temperature-dependent transitions in electrical conductivity.

In a later report, Ikalla extended his methodology by combining metal coordination and ionic interactions to functionalize polymers.²⁹ Zinc was coordinated to poly(4-vinylpyridine) containing dodecylbenzenesulfonate counterions (**45**). The

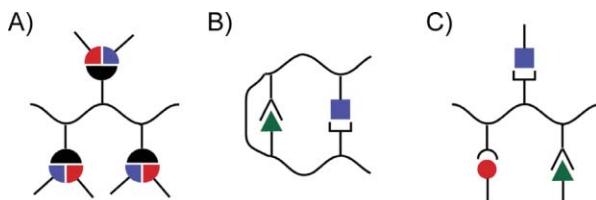


Fig. 16 Schematic display of different types of side-chain polymers based on multiple recognition motifs

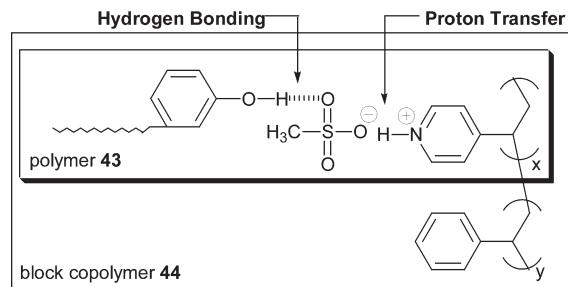


Fig. 17 Complexes formed as a result of hydrogen bonding and proton transfer, which are joined at each repeat unit of poly(4-vinylpyridine).

resulting supramolecular structure gave rise to a synthetically facile preparation method for multicomb polymeric assemblies (Fig. 18).

Late last year, Sleiman and co-workers reported the synthesis of self-complementary ABC triblock copolymers containing various block sequences of diacetamidopyridine, dicarboxyimide, and alkyl residues (Fig. 19).²⁶ These copolymers showed dramatic sequence dependent morphological changes in organic solvents. The strong morphological changes suggest that intramolecular folding of the complementary dicarboximide and diacetamidopyridine units could be taking place *via* hydrogen bonding.

In theory, the concept of multiple interactions along a polymer backbone is simple. However, the design, preparation and functionalization of systems containing more than one

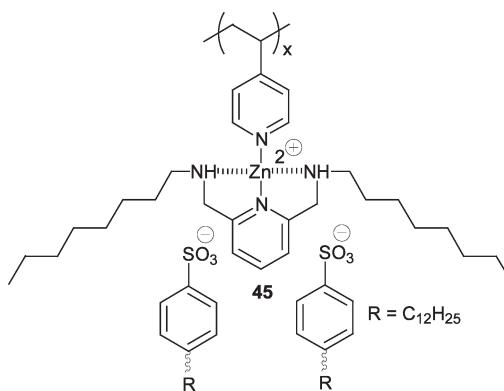


Fig. 18 Multicomb polymeric assemblies formed *via* simultaneous employment of metal coordination and ionic interactions.

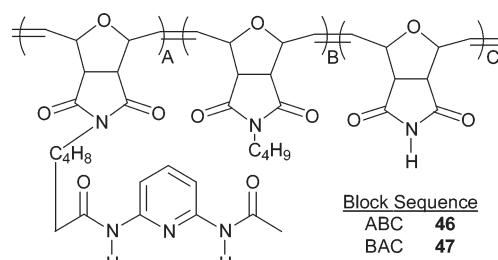


Fig. 19 ABC block copolymers containing diacetamidopyridine and dicarboxyimide hydrogen-bonding recognition units that are complementary to one another.

recognition motif can be quite complex. These systems must employ several stringent design criteria, including i) polymerization strategies that allow for defined copolymer formation, ii) sufficiently strong self-assembly motifs, iii) selective binding of each recognition motif for its partner in the presence of potentially competitive interactions, and iv) full solubility of resultant polymers that can be complicated by either the formation of ionic species or the polarity of many recognition motifs.

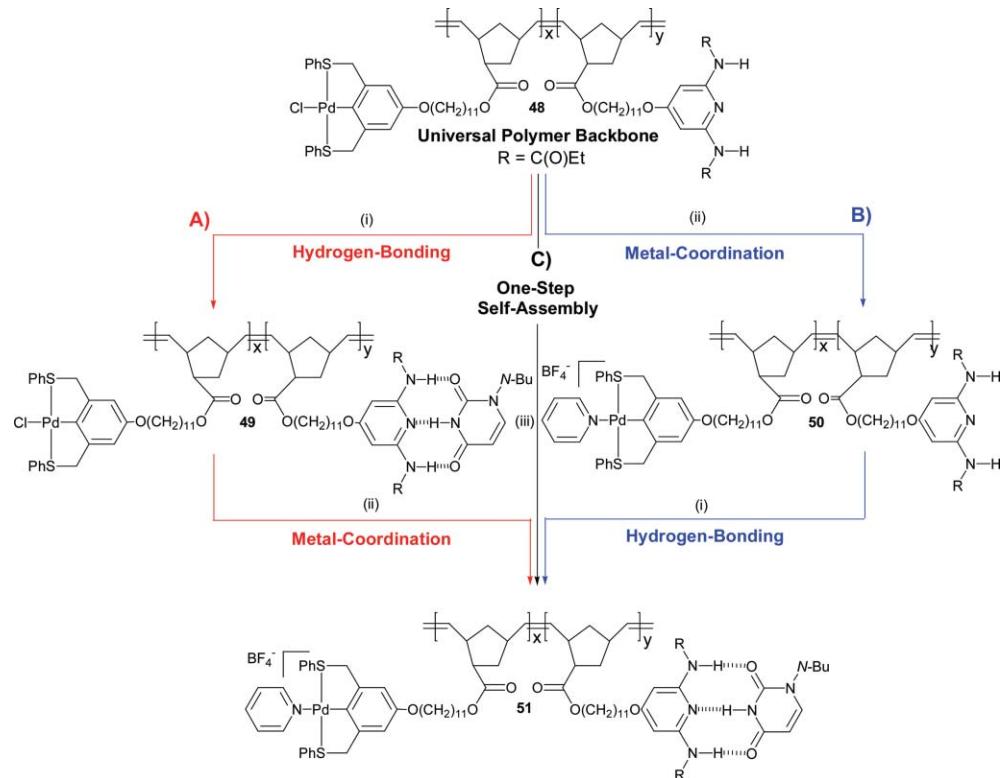
A first example of a system containing two discrete recognition units located along a polymer backbone designed to selectively and intermolecularly bind their respective complementary units, was published by Week and co-workers.²⁷ In this report, random copolymers possessing both metal-coordination complexes and hydrogen-bonding moieties were prepared. These new copolymers, appropriately called “universal polymer backbones”, could be rapidly functionalized with complete specificity of each recognition motif for its complementary partner (Scheme 7). This report introduced several new functionalization strategies. Here, a random copolymer (**48**) possessing Pd(II) SCS pincer complexes and diaminopyridine moieties was non-covalently functionalized using pyridine and butylthymine respectively. Three distinct functionalization methods were executed including i) directed self-assembly where each recognition motif was individually addressed to provide either hydrogen bonded or metal coordinated monofunctionalized polymers **49** and **50**, ii) multi-step self-assembly where polymer **48** was fully functionalized *via* a two-step sequential addition of complementary

units to form **51**, and iii) one-step orthogonal self-assembly, where both recognition units selectively bind to their complementary units in the presence of one another to form the fully functionalized polymer **51**. In all instances, quantitative self-assembly of the pyridine onto the Pd(II) and strong hydrogen-bonding interactions with association constants in the range of 500–600 M⁻¹ were observed. Furthermore, the physical properties of **51**, such as glass transition temperature and decomposition onset, were independent of the functionalization strategy employed.

Although this report only demonstrates the methodology for modular copolymer functionalization, the implications are far reaching. One could imagine an entirely new methodology for optimization of functional materials using this approach by giving the synthetic chemist a tool to examine each component of a polymeric material individually, or to investigate a variety of components and how they interact in the presence of each other, all without changing the properties of the original polymer backbone. Furthermore, the system allows one to synthesize multifunctionalized materials in seconds rather than months, and opens opportunities to employ combinatorial chemistry to materials science.

4 Conclusions and future perspectives

In the last decade, the field of supramolecular side-chain functionalized polymers changed from a curiosity to a mature area of polymer science. Based on the work by early pioneers such as Lehn and Fréchet, efficient methodologies towards the



Scheme 7 Functionalization strategies of the universal polymer backbone: A) Step-wise functionalization beginning with hydrogen bonding, B) with metal coordination and C) one-step multi-recognition site self-assembly. (i) *N*-butylthymine, CH₂Cl₂, (ii) pyridine, AgBF₄, CH₂Cl₂, (iii) *N*-butylthymine, pyridine, AgBF₄, CH₂Cl₂.

synthesis of supramolecular SCFPs that are based on a single non-covalent interaction have been developed. In particular hydrogen bonding has been used extensively with examples by a variety of groups. In contrast, the use of metal coordination as non-covalent recognition motif in SCFPs has just started to attract the attention of some research groups and important achievements should be expected in the future.

The outlook for supramolecular SCFPs as a sub-field of polymer science is promising. As outlined in this review, the fundamental principles of hydrogen-bonding based single SCFPs have been established and are well understood, whereas the use of metal coordination as non-covalent linkage is beginning to emerge in the literature. While these basic studies establish the methodology for the field, the use of other recognition units based on weak interactions such as Coulombic forces have to be developed and the proof of the full potential of supramolecular SCFPs has yet to be demonstrated. Most studies reported in the literature have been carried out in solution. However, the solid state properties of SCFPs are of utmost importance for the applicability of these materials and detailed studies towards a better understanding on how non-covalent interactions scale in the solid state, how they influence materials properties, and how they can be controlled have to be carried out. Furthermore, the influence of weak interactions on polymer processing as well as polymer morphologies and phase separation has to be addressed.

Another area of potential growth is in the use of supramolecular SCFPs in materials science. A number of promising leads are available in the literature. As discussed, the use of supramolecular SCFPs as liquid crystalline materials has matured in the last decade and other materials based on single functionalization methodologies may be forthcoming in the near future. Other advanced applications of supramolecular SCFPs for the synthesis and optimization of a variety of materials have been suggested, however optimized materials are not available. Promising areas include the synthesis of inorganic/organic hybrid materials, composite materials, biomaterials including drug delivery systems or biosensors, and electronic or photonic materials. Furthermore, the use of controlled phase separation could be used to synthesize well-defined three-dimensional polymeric structures that are otherwise impossible or hard to fabricate. A long-term goal of this field should be the integration of complex function such as enantioselective catalysis into well-defined three-dimensional structures that are synthesized using directional non-covalent interactions in the polymer side-chains with proteins and enzymes being the prime examples from Nature. Finally, it has to be demonstrated that materials prepared using non-covalent methodologies indeed possess advantages when compared to their covalent counterparts so that the often-mentioned concept of 'rapid optimization' via non-covalent interactions can be realized.

In contrast to single non-covalent SCFPs, only few reports are in the literature, which describe the use of multiple weak interactions to functionalize polymers in an orthogonal fashion and this concept has not been established in the larger polymer community. However, it is expected that this area will see tremendous growth as a result of its simplicity. This

concept has the potential to overcome some of the drawbacks of covalent copolymer synthesis including reagent incompatibility and lengthy synthesis. This technology will no doubt see continuing advances that will establish the methodology and its maturation will be dependent on its use and acceptance in materials applications. Based on recent creative leaps and advances in the field, the future looks to be promising and prosperous.

Acknowledgement

We gratefully acknowledge the support and enthusiasm of former and current group members and colleagues. Financial support has been provided by The Petroleum Research Fund, administered by the ACS, the National Science Foundation (ChE-0239385), the Office of Naval Research (MURI, Award No. N00014-03-1-0793), Halliburton Energy Services, and DuPont. MW gratefully acknowledges a 3M Untenured Faculty Award and an Oak Ridge Associated University Junior Faculty Enhancement Award.

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