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Supramolecular Polymerizations and Main-Chain Supramolecular Polymers

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ABSTRACT: The past few decades have seen a significant growth in the field of supramolecular polymerizations, in which (reversible) noncovalent interactions (e.g., hydrogen bonding, metal−ligand coordination, $\pi-\pi$ stacking, etc.) between (macro)monomeric units are utilized to build polymeric assemblies. These polymeric aggregates can exist in an equilibrium state between low and high molecular weight species, which in turn opens the door to a new matrix of properties. For example, such supramolecular polymers are potentially an interesting class of stimuli- or environmentally responsive, "smart" materials. Additionally, the establishment of an equilibrium during the assembly process imparts on the system the ability to "proofread" assemblies and, depending on the nature of the (macro)molecules, can allow efficient access to controlled, well-defined nanostructures. This Perspective will focus on the basic concepts of such supramolecular polymerizations, such as mechanism of assembly growth, and the effects of growth kinetics, phase segregation, and growth on the surface has on the assembly and properties of the resulting supramolecular polymers, highlighting these concepts with selected literature examples.

Introduction

Supramolecular chemistry has been described as "chemistry beyond the molecule"[1] where well-defined, noncovalent interactions play a key role in the assembly, conformation, and/or behavior of a system. Similarly, supramolecular polymers[2] can be aptly classified as polymeric systems that extend beyond the molecule and utilize noncovalent interactions to define their assembly, conformation, and/or behavior. Using such a definition, the field of supramolecular polymers can encompass a wide range of current research interests from the assembly of block copolymers[3] to protein folding and aggregation.[4] In this Perspective, however, we will focus on a smaller subset of such materials, namely the field of supramolecular polymerizations where reversible/dynamic noncovalent interactions control the self-assembly of (macro)monomers into larger polymeric structures. In these main-chain supramolecular assemblies, where the noncovalent interactions are part of the polymeric backbone, the resulting aggregates can often possess polymer-like properties. However, with such main-chain supramolecular polymers there exists an equilibrium process between monomeric, oligomeric, and polymeric species (assuming the absence of any kinetic traps, e.g., crystallization). Thus, for example, a monomer (A−A) which contains self-complementary binding units will, under the appropriate environmental conditions, spontaneously self-assemble into a linear supramolecular $(\mathrm{A-A})_n$-type polymer (Figure 1) as governed by the thermodynamics of the system. Such an assembly also possesses few irreversible termination processes, and the system's degree of polymerization (DP) is chiefly controlled by the binding constant, monomer concentration, and assembly mechanism (*vide infra*). The establishment of a dynamic equilibrium results in two principal properties exhibited by these supramolecular materials, namely stimuli-responsiveness and self-assembly of nanostructures, both of which can be difficult to attain using standard covalent polymers, and as such have shaped much of the research in this field.

The stimuli-responsive nature of such main-chain supramolecular polymers is derived from the ability to impact the dynamic equilibrium inherent in the system with external stimuli (e.g., temperature, chemical, pressure, light, etc.). Of course, response to an external stimulus is not a new property and has been achieved with a range of traditional polymers, e.g., electro-active polymers,[5] polymer solutions and gels capable of undergoing a phase transition,[6] liquid crystal polymers,[7] shape memory polymers,[8] and electro- and magneto-rheological fluids.[9] However, the sensitivity of noncovalent interactions to external stimuli combined with the typically large difference in macroscopic properties observed between monomeric/oligomeric and polymeric species results in supramolecular polymerizations as an ideal platform to access stimuli-responsive materials. Any environmental factor or stimulus that can influence the strength of the supramolecular interaction (i.e., the equilibrium or binding constant, K_a) between the (macro)monomer units will shift the monomer/oligomer/polymer equilibrium (Figure 2a), dramatically impacting the degree of polymerization of the aggregate and in turn drive significant changes in the materials' properties. For example, increasing the temperature of a supramolecular system will usually result in depolymerization of the aggregate (although depending on the nature of the supramolecular aggregate an opposite effect can be observed *vide infra*). A similar reduction in molecular weight can be induced by decreasing the system's concentration or introducing a competitive binder. Thus, a material formed via a supramolecular polymerization process innately has the potential to behave in a stimuli-responsive manner. Of course, the other key related consideration in such dynamic systems is the formation of macrocycles[10] and the presence of ring−chain[11] or ring−ring equilibria,[12] which will impact the size of the polymeric aggregates that can be obtained. As with all equilibrium polymerizations it can be expected, and theory predicts, that a percentage of the chains will be

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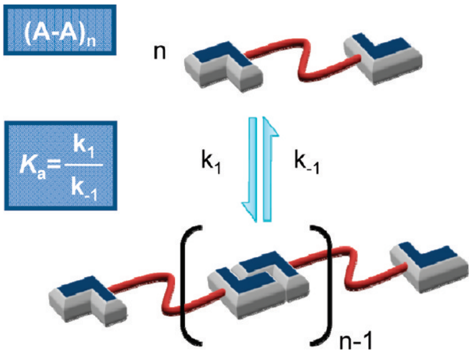


Figure 1. Formation of a main-chain supramolecular polymer highlighting the dynamic equilibrium and kinetics of a supramolecular polymerization.

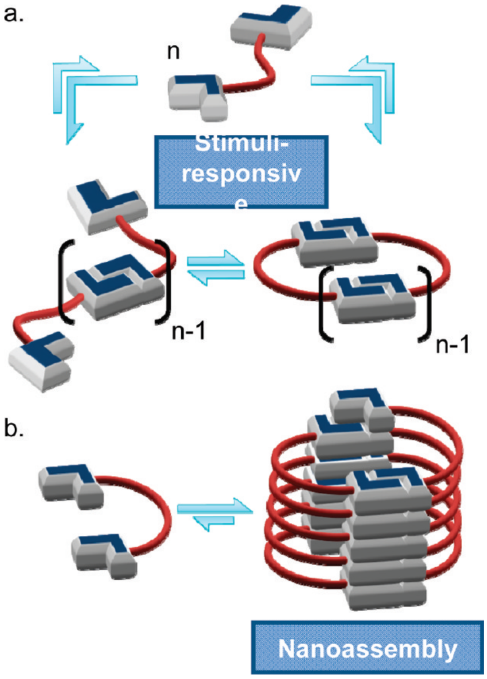


Figure 2. Supramolecular polymerizations can give access to (a) stimuli-responsive behavior and/or (b) thermodynamically controlled self-assembled nanoassembles structures.

macrocyclic. The exact distribution of rings verses chains will depend on a number of factors,[13] including, monomer shape (e.g., bent vs linear), length and flexibility of the core, strength of the binding motif, concentration, temperature (*vide infra*), and even the orientational specificity of the binding group.[14] It is also possible for competition to occur between more than one type of linear supramolecular polymeric architecture that are assembled from the same monomer. Bouteiller and co-workers recently described the ability of bis-urea monomers to self-assemble into either a single-chain aggregate or a more complex tubular architecture, dependent on the solvent, temperature, and concentration of the system.[15]

The reversible nature of the molecular assembly opens the door to another key attribute offered by such systems, namely the ability to form thermodynamically controlled assemblies. In this case, ideally, the (macro)monomers are designed (e.g., through structural and noncovalent considerations) to result in the self-assembly of predominantly one type of noncovalent species (Figure 2b). As the assembly process is reversible and the formation of products is in continuous equilibrium, the system undergoes “error checking” or “proofreading” of thermodynamically unstable assemblies, resulting in their conversion into (ideally) the most thermodynamically stable assemblies. As such, supramolecular polymerizations can be a powerful bottom-up approach to access complex nanoarchitectures (*vide infra*).

There are potentially a variety of ways to access polymeric architectures, where the supramolecular motif is part of the main chain, most of which have analogies to covalent polymerizations. The simplest conceptual class of (macro)monomer is one that has self-complementary binding units (resulting in a dimeric supramolecular motif) covalently attached to either end of a core which thus results in a self-assembling $(A{-}A)_n$ polymer (Figure 1). If the supramolecular motif used in the assembly of the polymer is unsymmetric (i.e., consists of two different complementary binding units, A and B), then the supramolecular polymer will only be formed to any appreciable extent when both of these

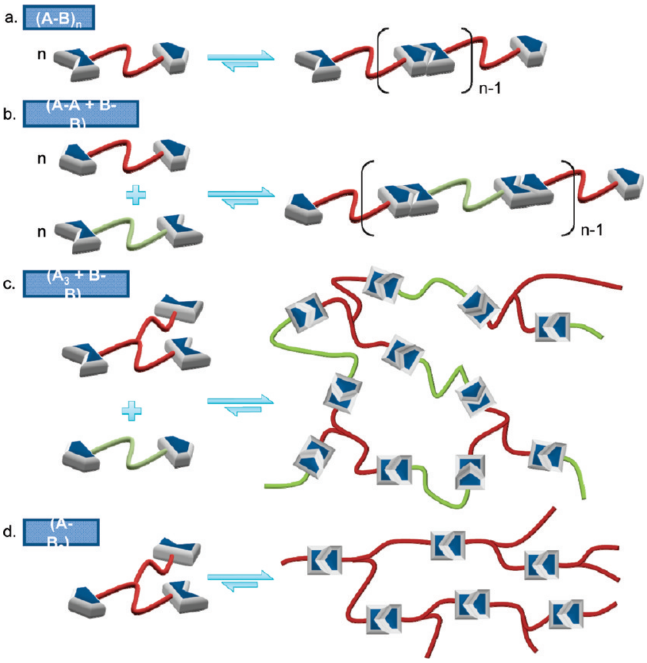


Figure 3. A selection of different main-chain supramolecular polymers can be accessed depending on the nature of the binding motif and the monomer. For example, (a) a A$-$B supramolecular polymer, (b) a A$-$A$\cdot$B$-$B alternating supramolecular block copolymer, (c) a $A_3\cdot$B$-$B supramolecular network, and (d) a A$-B_2$ hyperbranched supramolecular polymer.

complementary units are present in equal proportions. A heteroditopic monomer, in which both heterocomplementary units are placed on the same monomer, results in a self-assembling $(A-B)_n$ polymer (Figure 3a). However, homoditopic monomers, in which only one of the heterocomplementary units is placed on the ends of the monomer (e.g., A$-$A or B$-$B), will only exhibit polymer-like properties upon mixing, ideally equal molar ratios of the two complementary monomers (Figure 3b). Of course, if oligotopic (rather than ditopic, e.g. $(A)_m$, $m > 2$ instead of A$-$A) monomers are used, then the assembly results in the formation of cross-linked or network-like architectures (Figure 3c). Alternatively, an A$-B_2$ monomer will yield hyperbranched supramolecular systems as shown in Figure 3d.

Conceptually, the supramolecular polymerizations outlined above can utilize (a combination of) any of the wide range of noncovalent interactions and effects, such as hydrogen bonding, $\pi-\pi$ stacking, metal coordination, electrostatics, hydrophobic effects, phase segregation, etc., that are available. The exact noncovalent interaction(s) selected and utilized depends on a number of different factors, such as the environment (aqueous, organic solvent, solid state, etc.) of the assembly process and/or the strength and kinetics of the interaction required. As such, over the years a wide range of supramolecular motifs have been developed for and utilized in supramolecular polymerizations. Figure 4 shows two commonly utilized supramolecular motifs which take advantage of different noncovalent interactions. The urediopyrimidone dimer (Figure 4a) is an example of a four-hydrogen-bonded array that will assemble into an $(A-A)_n$-type polymer, while the 2:1 terpyridine/metal ion complex (Figure 4b) allows access to $(A-A\cdot B-B)_n$ metallo-supramolecular polymers[16] where the hexacoordinate metal ion can be considered as the B$-$B complementary monomer to a ditopic, ligand end-capped (macro)monomer (A$-$A).

Assembly Growth Mechanisms

There are a number of reasons why the two motifs shown in Figure 4 have proved very popular in the field of supramolecular

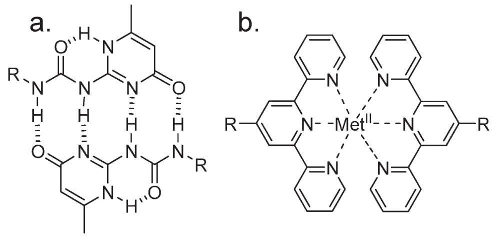


Figure 4. Chemical structures of two common motifs used in supramolecular polymerizations (a) 2-ureido-4-[1*H*]pyrimidone dimer and (b) 2:1 terpyridine/metal ion complex.

polymerizations, which include their ease of accessibility and their large binding constants. Both the motifs can exhibit binding constants $> 10^6$ M^{-1}, which is an important consideration if one is trying to access large polymeric aggregates. To better understand this, the different possible growth mechanisms used to access a given assembly need to be considered.[17] Figure 5 shows a schematic of the degree of polymerization dependence versus monomer concentration for three possible growth mechanisms, namely the multistage open association (isodesmic) mechanism, nucleation$-$elongation (or helical growth) mechanism, and growth coupled to nematic orientation (or open supramolecular liquid crystal, SLC). The following discussion in this Perspective will only summarize the basic concepts of these growth mechanisms (more detailed descriptions and discussions can be found elsewhere in the literature[17,18]).

Conceptually, the simplest growth mechanism is the multistage open association mechanism (MSOA), which is essentially a closed reversible step-growth process where the binding constant is independent of the molecular weight (i.e., no cooperation). Thus, it can be calculated that, assuming no ring formation, the DP will be approximately proportional to $(K_a[M])^{1/2}$, where K_a is the binding constant and [M] is the total concentration of monomer units.[19] As can be seen in Figure 5a, the MSOA mechanism results in a steady, gradual growth in molecular weight (or DP) upon an increase in the concentration of monomer units.

If this growth mechanism is followed, then large K_a's will be required to obtain aggregates of significant molecular weight, especially in solutions where [M] is not maximized. Thus, this has led to the development of a range of supramolecular motifs which exhibit large binding constants ($>10^6$ M^{-1}).[20-22] As mentioned above, the quadruple hydrogen bonding 2-ureido-4-[1*H*]pyrimidone (UPy) (shown as its supramolecular dimer in Figure 4a) developed by Sijbesma and Meijer is one of the most elegant and successfully utilized hydrogen-bond motifs for supramolecular polymerizations.[23] For example, as a result of the strong dimerization of the UPy motif ($K_{dim} > 10^7$ M^{-1} in chloroform), it is possible to obtain highly viscous chloroform solutions of the UPy end-capped poly(ethylene butylene) macromonomer (**1**, $M_n = 4100$, Figure 6a). Macromonomer **1** also shows dramatically enhanced mechanical properties in the solid state compared to the unfunctionalized poly(ethylene butylene) backbone (**2**, $M_n = 3500$).[24] For example, the low molecular weight unfunctionalized polymer with hydroxyl end groups (**2**) is a viscous oil at room temperature while the UPy end-capped **1** can form stand alone flexible thermoplastic films (Figure 6b). Dynamic melt viscosity experiments were performed on the functionalized and unfunctionalized polymers and show an increase of 5 orders of magnitude in the zero shear melt viscosity for the supramolecular polymer (**1**) over the nonfunctionalized macromonomer **2** at low frequencies (Figure 6c). Furthermore, a strong temperature and frequency dependence of the melt viscosity is observed for **1** consistent with the reversible, dynamic nature expected for such a supramolecular polymer.

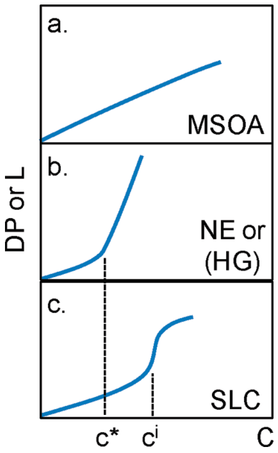


Figure 5. Schematic representation of the degree of polymerization (DP) (or length, *L*) versus monomer concentration (*C*) for different supramolecular growth mechanisms: (a) multistage open association (MSOA), (b) nucleation−elongation (NE) or helical growth (HG), and (c) growth coupled to nematic orientation or open supramolecular liquid crystal (SLC). Note the concentration at which helical growth begins (c^*) is generally smaller than that of mesophase formation (c^i).

An interesting alternative demonstration of the reversible nature of such a supramolecular polymerization was also reported by Meijer and co-workers.[25] In this case they added 0.1 equiv of the monotopic protected UPy derivative **4** to a chloroform solution of UPy end-capped ditopic monomer **3**. The protecting *o*-nitrobenzyl group on **4** significantly reduces the hydrogen-bonding capability of this molecule. However, exposure to UV irradiation removes the protecting group from compound **4**, exposing the four-hydrogen-bonding array of the UPy monomer **5**. **5** can now competitively bind with **3** and thus acts as a chain terminator for the supramolecular polymer $(\mathbf{3})_n$. This photoinduced depolymerization process of $(\mathbf{3})_n$ can be followed by the dramatic drop (of more than 5 times) in the relative viscosity of a solution containing $(\mathbf{3})_n$ and **4** upon exposure to light (Figure 7b). This system nicely demonstrates the dynamic equilibrium present in supramolecular polymers and how this may be influenced to yield stimuli-responsive properties, specifically, in this particular system an irreversible change in viscosity upon exposure to light.

As can be seen from the example above, the presence of chain stoppers (which may come from some monofunctionalized monomers or as a stoichiometric imbalance in an A−A/B−B system) can have a drastic effect on the size of the resulting polymeric aggregates formed through the MSOA mechanism. However, the controlled use of strong associating chain stoppers can be beneficial. For example, as one might expect addition of a chain stopper can be used to control the molecular weight of the polymeric aggregate (akin to using a chain-transfer agent in covalent polymerizations). Furthermore, as both Bouteiller[26] and Knoben[27] have shown, addition of a (small amount of) chain stopper can change the concentration dependence of the aggregate. In a stopper-free system the chain ends of the growing chain are always active, and the polymer continues to increase in size with concentration (at the same time the number of chains decreases). However, in a system with chain stoppers present the molecular weight of the aggregate will increase only up to a certain concentration (C_t), at which point the majority of the chains will be terminated with a chain stopper. Thus, above C_t the aggregates cannot increase in size, and the molecular weight of the aggregate stays constant with increasing concentration.

The systems discussed up to this point utilize the MSOA mechanism described previously, the fundamental feature of which being that the binding constant of the growing

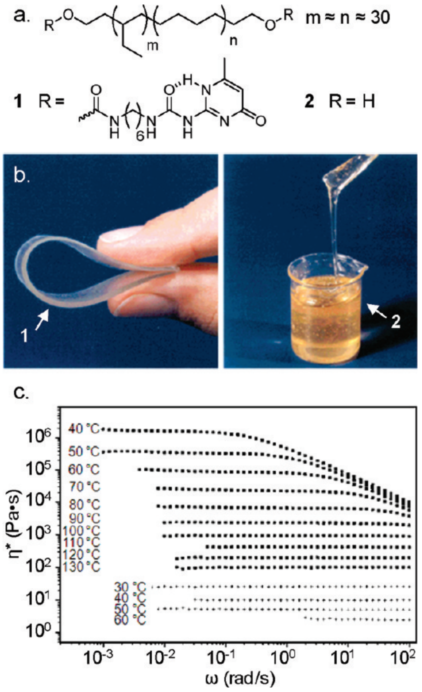


Figure 6. (a) Hydrogen-bonding macromonomer **1** which utilizes the UPy motif and the unfunctionalized analogue **2**. (b) Visual comparison of **1** (left) and **2** (right) at room temperature. (c) Dynamic melt viscosity at different temperatures of **1** (■) and **2** (+). Reproduced with permission from ref 24. Copyright 2000 Wiley.

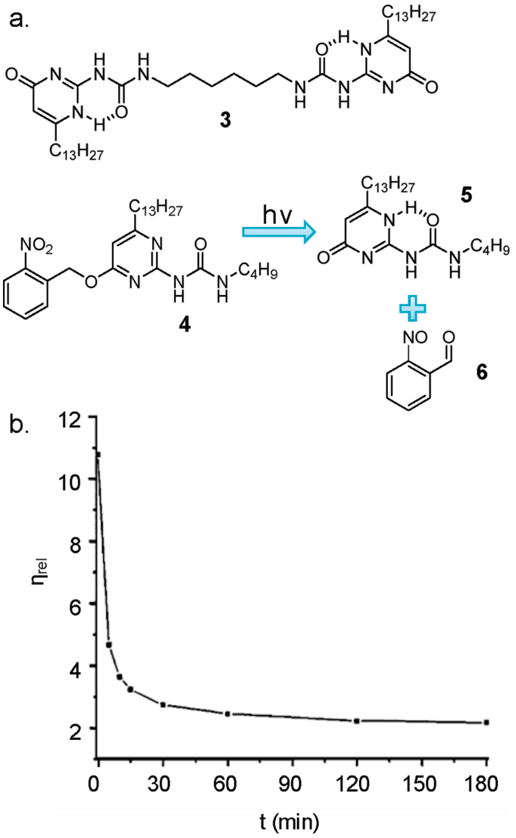


Figure 7. (a) Supramolecular monomer **3**, and a competitive binder before (**4**) and after (**5**) UV irradiation. (b) Relative viscosity of the system (40 mM solution of **3** in CHCl_3 with 0.1 equiv of **4**) upon exposure to UV irradiation over time. Reproduced with permission from ref 25. Copyright 1998 Royal Society of Chemistry.

supramolecular polymer is unaffected by molecular weight. However, if an additional supramolecular interaction (typically $\pi-\pi$ stacking, hydrophobics, and/or van der Waals forces) occurs in the system upon reaching a sufficient degree of polymerization, then an increase in the binding constant can occur, i.e., $K_{a'} > K_a$ (Figure 8).[17,28] Such a system is said to undergo supramolecular polymerization via the nucleation–elongation (or helical growth) mechanism.[29] In this case, one or several initial binding events (nucleation) must occur, using e.g. an MSOA growth mechanism (K_a), before the aggregates get large enough to allow the secondary interaction (or a conformational preorganization effect[30]) to enhance the binding constant ($K_{a'}$) and therefore enhance the growth of the chain (elongation). Thus, in this mechanism there is a concentration C^* (Figure 5b) where a jump in the degree of polymerization is observed. In many systems, a helical geometry is best suited to take advantage of the secondary binding forces, hence the term “helical growth”. Since polymeric aggregates (above the nucleation size) possess a higher binding constant ($K_{a'}$), monomers preferentially add to the growing chains instead of establishing new chains. In this manner, supramolecular polymers formed via a nucleation–elongation pathway are the noncovalent analogues of chain-growth polymers; existing polymeric entities grow by preferential addition of monomer (instead of oligomers combining to gradually form high molecular weight polymers as in the step-growth mechanism). As a result, the nucleation–elongation growth mechanism can result in a bimodal distribution with high molecular weight aggregates present at the same time as monomeric species. Thus, it is easier to attain high molecular weight aggregates with such a mechanism which makes the system more robust. For example, an A–A/B–B system will still form high molecular weight aggregates (along with monomers) even if the monomer stoichiometry deviates from the ideal 1:1.[31]

Meijer and co-workers have developed a hydrogen-bonded self-complementary low molecular weight ditopic monomer[32] that exemplifies the growth of a columnar polymeric aggregate aided by secondary interactions (in this case solvophobic effects) (Figure 8). The ditopic monomer **7** utilizes ureidotriazines as a self-complementary quadruple hydrogen-bonding motif that can form random coil supramolecular polymers in chloroform solutions. However, in dodecane solvophobic effects come into play, and large columnar aggregates (length of 10 and 19 nm for 0.2 and 1.0 wt % of **7**, respectively) can be observed by small-angle neutron-scattering experiments. Using chiral alkyl chains attached to **7**, circular dichroism (CD) spectroscopy revealed (by the Cotton effect) the helical nature of columnar aggregates. Subsequently lowering the concentration of monomer by 3 orders of magnitude (from 10^{-3} to 10^{-6} M) results in the Cotton effect ($\Delta\varepsilon$) dropping by only half, suggesting that even by drastically decreasing the monomer concentration within this concentration regime the majority of the molecules are still part of the helical columns. At higher concentrations (above 0.024 M for **7**), long-range ordering (liquid crystallinity) is observed as the columns form a lyotropic mesophase; increasing concentration further into the bulk reveals that the columns of **7** are pseudohexagonally packed in a rectangular lattice. This particular example shows how an understanding of the supramolecular interactions (in this case hydrogen-bonding and solvophobic effects) at play during the assembly can be used to access controlled nanoassemblies, in this case columnar aggregates as opposed to a coil polymeric assembly.

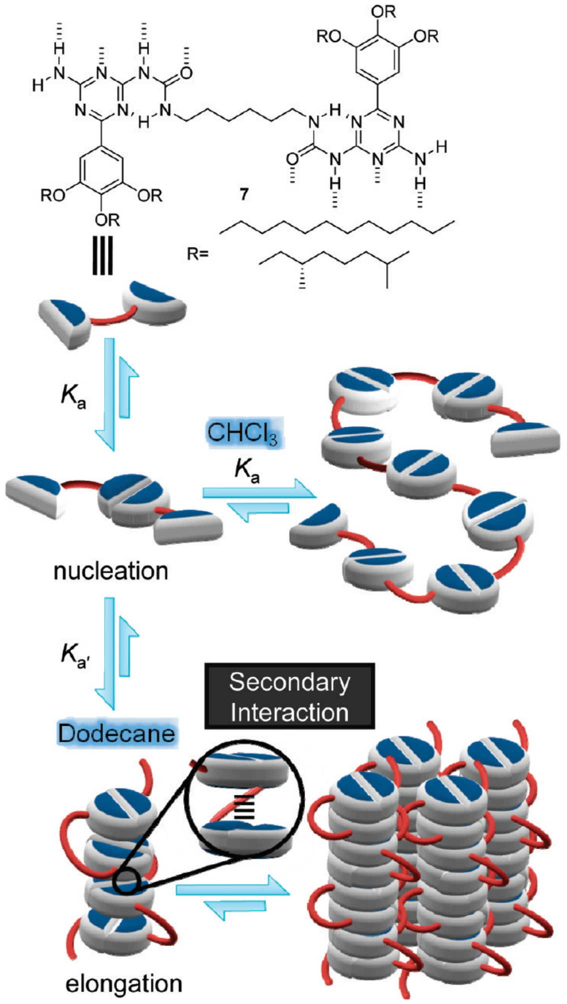


Figure 8. Schematic representation of the assembly of **7** in chloroform and dodecane. In chloroform **7** forms random coil main-chain supramolecular polymers; however, in dodecane secondary interactions aid the growth of **7** resulting in large helical columnar aggregates which can further organize into geometrically packed structures.

As seen with the lyotropic and thermotropic properties of compound **7** (*vide supra*), supramolecular systems can display liquid crystallinity resulting from varying degrees of spatial and orientational ordering imparted by intermolecular interactions. Indeed, many of the earliest successful supramolecular polymers from Lehn,[33] Fréchet and Kato,[34] and Griffin[35] exhibited liquid crystalline (LC) behavior while utilizing a range of supramolecular motifs. Conceptually, the growth of the polymeric assembly can be coupled to the formation of a liquid crystalline phase, i.e., the open supramolecular liquid crystal mechanism.[36] Thus, for example, in a lyotropic system as concentration is increased, the adoption of long-range order can coincide with an enhancement in the growth of noncovalent assemblies. In such a growth-coupled-to-orientation process another growth mechanism (e.g., the MSOA mechanism) will be dominant until the critical concentration (c^i) for nematic order is reached,[37] at which point the long-range order results in a sudden increase in DP of the aggregate (Figure 5c) which can be identified by a sudden increase in the viscosity when the nematic phase appears. However, such a growth mechanism can be difficult to confirm,[38] especially given that liquid crystalline behavior can occur without it being linked to supramolecular growth. More studies into open SLCs and the continued development and refinement of theoretical models are required in order to better understand this growth mechanism and to use it to design *a priori* a supramolecular system that utilizes such an assembly mechanism.

As with the main-chain supramolecular polymers shown in Figure 3, there are numerous combinations of mesogens and architectures that can be classified as supramolecular liquid crystalline polymers (SLCPs).[39] One interesting subclass of the SLCPs are those in which the supramolecular motif is the mesogenic moiety (the system does not exhibit liquid crystallinity

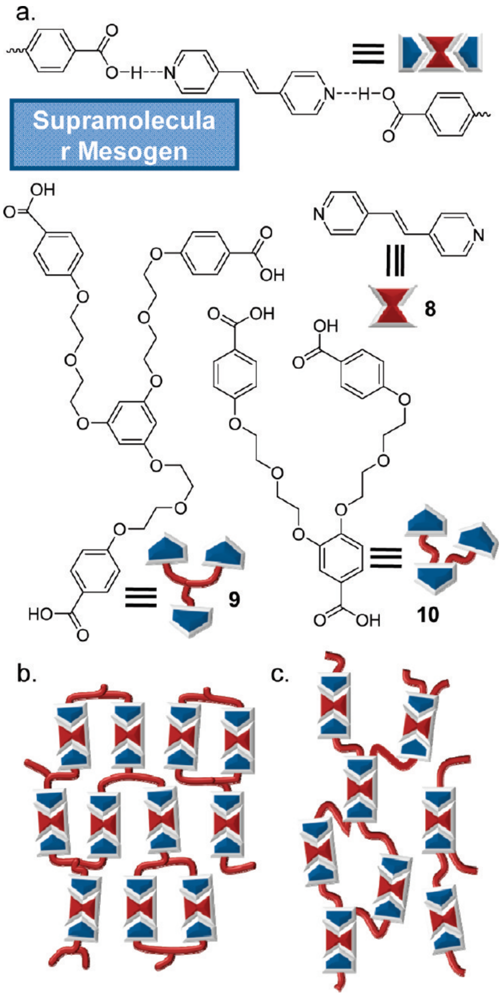


Figure 9. (a) Supramolecular mesogen formed by hydrogen bonding of **8** with benzoic acid moieties. Schematics of (b) smectic networks formed by combination of **8** with **9** and (c) nematic networks formed by combination of **8** with **10**.[41]

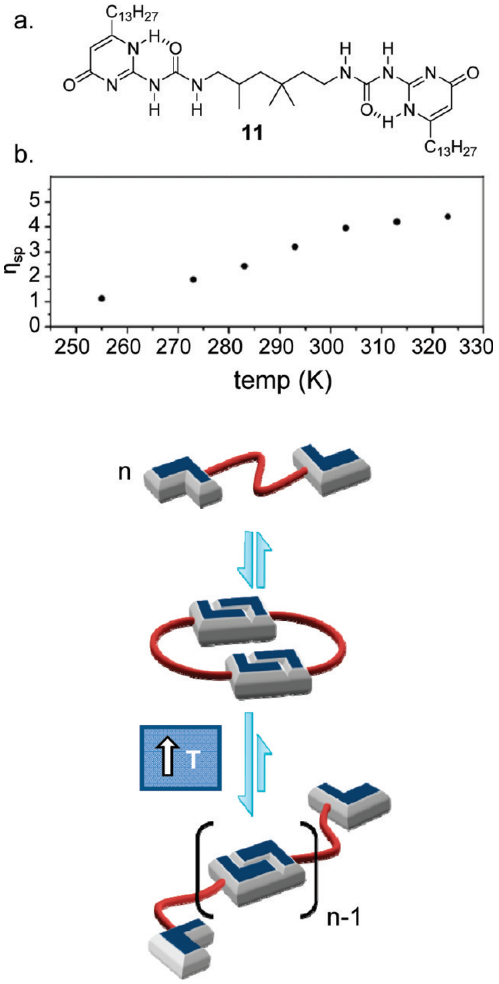
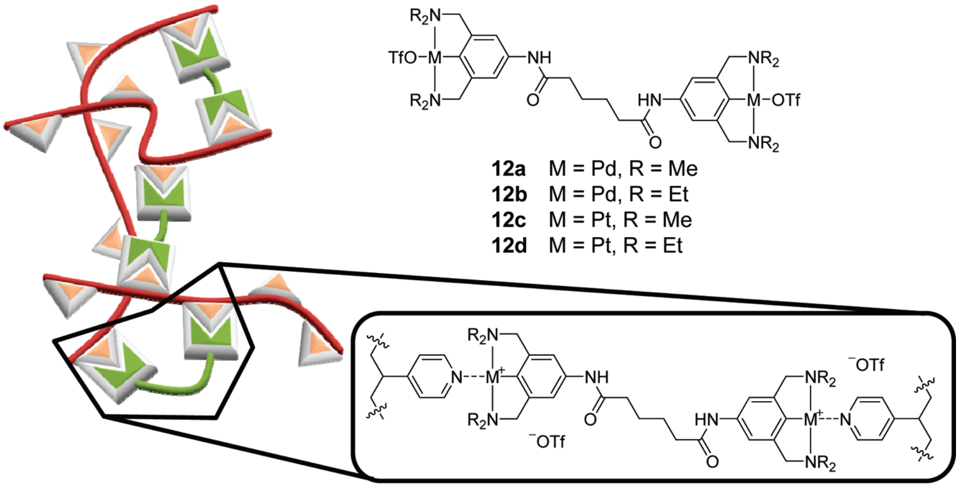


Figure 10. (a) Homocomplementary UPy monomer **11**. (b) Specific viscosity versus temperature for **11** (145 mM in $CHCl_3$) and a schematic of monomer dimerization and ring-opening to form the main-chain supramolecular polymer. Data taken from ref 43.

without significant supramolecular interaction). An example of such a mesogenic supramolecular motif is the combination of (*trans*-l,2-bis(4-pyridyl)ethylene) **8** with 2 equiv of alkoxybenzoic acids (Figure 9a).[40] Using this motif, Kato and co-workers[41] developed a system (Figure 9) where combinations of the nonmesogenic trifunctional benzoic acid-based hydrogen-bond donors (**9** and **10**) and the nonmesogenic bifunctional pyridyl-based hydrogen-bond acceptor (**8**) assemble into supramolecular liquid crystalline networks whose thermal properties are controlled (at least in part) by the shape of the assembling monomers. The symmetrical trifunctional monomer **9** forms a monotropic smectic A phase with **8** upon cooling (I 176 °C S_A 156 °C K), while the less symmetrical trifunctional monomer **10** forms an enantiotropic nematic phase (e.g., on cooling I 200 °C N 87 °C G) under the same mixing conditions with **8**. It is argued that **8·9** favors smectic phases since **9** is able to adopt a more parallel, Y-shaped geometry (Figure 9b), while **10**, with fewer degrees of freedom, supports a less ordered nematic phase in the complex (Figure 9c). The range of behavior seen between the two sets of supramolecular complexes nicely illustrates the changes in properties of such supramolecular materials that can be attributable to small changes in the structure of self-assembling monomer units. The supramolecular nature of the mesogenic motif is arguably a key factor in the formation, stabilization, and dynamic behavior of these liquid crystalline networks and highlights the potential of such supramolecular materials to access self-organized functional structures.

Ring-opening polymerizations are another large class of reactions that are used to access covalent polymers. Conceptually, a similar process should be applicable to main-chain supramolecular polymers. Small cyclic ring-opening polymerizations are usually driven by ring strain, and in a thermodynamically controlled supramolecular assembly process access to small strained ring assemblies will be difficult. An alternative form of ring-opening polymerizations involves the entropically controlled ring-opening of unstrained macrocyclic monomers, which are accessible using supramolecular interactions and as such the ring-opening polymerization of macrocyclic assemblies should be feasible.[42] Such a system was recently demonstrated by Sijbesma and Meijer.[43] Compound **11** has two UPy end groups attached by a C6 alkyl chain possessing three methyl side groups, and in chloroform this compound exhibits high temperature and concentration sensitivity. The methyl groups encourage the formation of low molecular weight macrocyclic species at low concentrations and temperatures. Upon increasing the concentration above 90 g L^{-1} (ca. 113 mM), a more significant increase in viscosity is observed with increasing concentration, which is ascribed to the ring-opening polymerization of supramolecular cyclic species of **11**. Furthermore, solutions of **11** show interesting thermal-sensitive properties in that they exhibit a floor temperature (which is to be expected from such an entropically controlled polymerization), below which cyclic species are dominant and above which ring-opening polymerization occurs. Increasing the



Compound	K_a [M^{-1}]	k_{ex} [s^{-1}]	η [Pa s]	K_a [rel]	k_{ex}^{-1} [rel]	η [rel]
12a	35	≈1100	6.7	1.2	0.014	0.012
12b	29	15	550	1	1	1
12c	8000	0.026	240,000	280	600	440
12d	4000	0.0006	>240,000	140	25,000	>440

Figure 11. Schematic of the supramolecular network formed between poly(vinylpyridine) and the metallopincers **12a**−**12d**. Table illustrates absolute (left columns) and relative (right columns, normalized to **12b**) association constants (K_a) and exchange rates (k_{ex}) of the metallopincers with pyridine in DMSO and the viscosities (η) of metallopincers when combined with poly(4-vinylpyridine) (100 mg/mL in DMSO, 5% functional group equivalent relative to poly(4-vinylpyridine)).[44]

temperature of a 145 mM solution of **11** in $CHCl_3$ from room temperature results in an increase in specific viscosity (Figure 10b), consistent with the entropically favorable opening of the macrocyclic aggregate to form the supramolecular polymer. Increasing the concentration of the solution decreases the temperature at which the maximum viscosity is observed, indicating the competition between the ring-opening driven polymerization and the thermally induced decomplexation of the supramolecular motif. The competition results in an unusual interplay between viscosity, temperature, and concentration in this stimuli-responsive system.

Kinetics

A discussion of only the growth mechanisms and their relation to the binding strength of supramolecular polymers covers just one set of key parameters that must be considered in this field. A second set of key parameters are the exchange rates, namely the rates of complexation (k_1) and decomplexation (k_{-1}), the ratio of which is, of course, the binding constant, K_a (= k_1/k_{-1}) (Figure 1). Thus, it could be expected that, even if the binding constant (or ratio of k_1 and k_{-1}) was the same, a supramolecular polymer assembled through a binding motif with slow complexation/decomplexation rates will behave very differently from one assembled with a dynamic, fast-exchanging supramolecular motif. The major problem here is that, in general, it is difficult to separate out these two effects for most supramolecular motifs, that is, usually an increase in binding constant also comes along with a decrease in the exchange rates. However, Craig and coworkers[44] recently developed a supramolecular motif, pyridine/metallopincers (Figure 11), in which the exchange rates could be varied without significantly changing the binding constant and have used it to demonstrate the important role the binding rate has on the properties of a supramolecular system.

The binding of pyridine moieties to the metallopincers (**12a**−**12d**) depends not only on the metal ion but also on the R group attached to the benzyl amines. Most interestingly, while changing the R group from methyl to ethyl does not drastically affect the strength of the pyridine/Met^{II} interaction, the rate of exchange decreases by ca. 2 orders of magnitude. Thus, using this binding system, Craig prepared a series of supramolecular network organogels comprised of poly(vinylpyridine) (PVP) dissolved in dimethyl sulfoxide (DMSO) cross-linked with either bis-Pd^{II}- or Pt^{II}-pincer compounds (**12a,b** and **12c,d**, respectively, Figure 11). Addition of the more dynamically labile 5% **12a**·Pd^{II} cross-linker to a PVP solution results in a viscous material (η = 6.7 Pa s), whereas the corresponding supramolecular network PVP **12b**·Pd^{II}, formed with the slower exchanging cross-linker, is a gel (η = 550 Pa s). Further studies on these materials and their more thermodynamically and kinetically stable Pt^{II} analogues demonstrate that it is the decomplexation rate of the metal binding motif (and not the binding constant) that is responsible for the observed change in viscosity. This nicely highlights the importance of kinetics in dictating the properties of supramolecular polymers and suggests that "slower" binding kinetics means "stronger" materials.

Supramolecular Polymers and Phase Segregation

The nature of the main-chain supramolecular polymer means that the backbone will consist of alternating sections of the supramolecular motif and the core of the macromonomer. As such, it is possible that these systems can behave like AB multiblock copolymers and exhibit phase segregation between the binding motif and the core.[24,45] This raises the interesting question of how might such additional assembly in the solid state influence the physical properties of the films. For example, in metallosupramolecular polymers (MSPs) if the core consists of a "soft" unit, such as poly(tetrahydrofuran)[46] or poly(ethylene glycol),[47] and the metal−ligand complex is a "hard" ionic, aromatic species, e.g., complexes of 2,6-bis(1′-methylbenzimidazolyl)pyridine (Mebip) or terpy, then the different segments along the backbone of the MSP can phase segregate. This phase segregation can result in physical cross-linking (Figure 12a) occurring within the films potentially leading to elastomeric properties. Beck et al.[46] synthesized **13**, a system utilizing the Mebip$_2$·Zn^{II} motif (Figure 12b). X-ray (WAXS) and DMTA data are consistent with the presence of a cross-linking phase-segregated morphology (probably lamellar) which is further

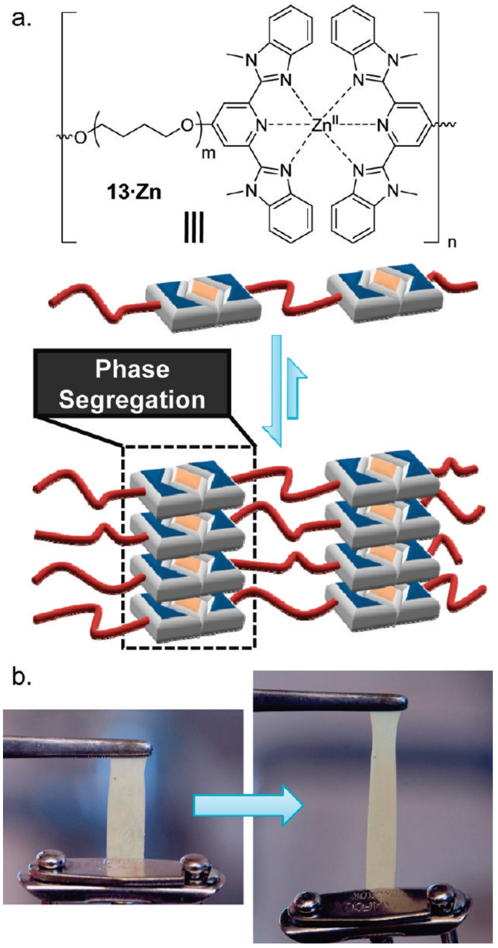


Figure 12. (a) Structure of a metallo-supramolecular polymer **13**$\cdot$Zn$^{\mathrm{II}}$ and the proposed AB multiblock-like phase segregation present in the solid state. (b) Pictures highlighting the elastic nature of the metallo-supramolecular polymer **13**$\cdot$Zn(ClO$_4$)$_2$.

backed up by the elastomeric behavior exhibited by these films (Figure 12c) at room temperature. This nicely demonstrates that the physical properties can be influenced by phase segregation of a main-chain supramolecular polymer, i.e., in this case through physical cross-linking by the "hard" supramolecular motif.

The above example shows what can happen when phase segregation occurs within a polymeric aggregate that is formed using a strong supramolecular binding motif. An alternative approach is to use phase segregation in conjunction with supramolecular motifs that have small binding constants. Thus, polymer-like properties may be attainable with low molecular weight compounds in which a soft core segment has weakly interacting hard segments attached at both ends (Figure 13a).[48−51] If phase segregation occurs, the effective molarity of the chain ends would be greatly increased,[52] thus enhancing their degree of interaction. Additionally, the presence of supramolecular interactions may aid phase segregation. Using this concept, Sivakova et al.[53] developed two low molecular weight ($<$2000 g/mol) polymers **14** and **15**, consisting of modified nucleobase moieties attached to either end of a low molecular weight poly(tetrahydrofuran), which show free-standing film forming capabilities (Figure 13b). In this case, these macromonomers can be considered as an ABA triblock copolymers, where the A units are the supramolecular motifs and the B unit is the soft poly(THF) core,[54] and the incompatibility of the terminal blocks (or supramolecular moieties) forces them to separate from the core polymer matrix. As such, a physical network architecture is formed with the "hard" or terminal phase composing the nodes or cross-links of the network. In the above systems phase segregation allows the use of weak H-bonding to access films that exhibit high thermal-responsive behavior. In this case, ideally, the H-bonding motif (although relatively weak in solution) is effectively strong at room temperature (i.e., slow reversibility) since the "hard" H-bonding phase is below its T_g or T_m kinetically trapping the chain ends. Upon transitioning across this T_g or T_m, the dynamics of the hard phase increases dramatically, and fast exchange of supramolecular moieties between phase-segregated regions can occur. The rate of exchange or "hopping" of chain ends (Figure 13c) is thought to be a key mechanism governing the physical characteristics of such dynamic networks. A combination of rheology and FT-IR data suggests that large drops in the modulus of these materials with temperature are more consistent with an increase in the hopping rate rather than simple decomplexation of the supramolecular motifs. As was the case with the metallo-gel systems studied by Craig (Figure 11), evidence was found that it was the disengagement rate of the supramolecular motif from the hard phase (which in this case is related to not only the k_{-1} of the motif but also to the T_g or T_m of the hard phase) that governed the rheological properties of these systems. Conceptually, the use of phase segregation allows access to dynamic supramolecular networks using weakly interacting supramolecular motifs and offers an alternative approach to highly stimuli-responsive materials.

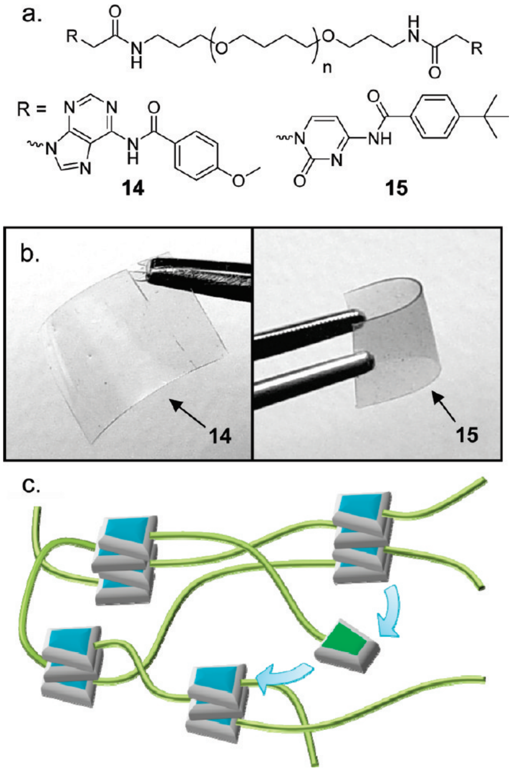


Figure 13. (a) Structures of adenine and cytosine end-capped poly(tetrahydrofuran) compounds (**14** and **15**, respectively), (b) picture of the stand-alone films of **14** and **15** after melt processing, and (c) idealized phase-segregated morphology in the solid state and proposed chain-end hopping mechanism present in these dynamic networks. Pictures taken from ref 53.

Phase separation may also play an important role in very different types of systems. For example, 2,6-bis(1′-methylbenzimidazolyl)pyridine (Mebip) ligands attached to the ends of a penta(ethylene glycol) core (**16**) result in the formation of metallo-supramolecular gels in acetonitrile upon the addition of transition metal with or without lanthanide metal ions.[55] These gels were shown to exhibit multiple stimuli-responsive behaviors, including thermo-, chemo-, and mechanical responses as well as exhibiting fluorescence properties. Under appropriate conditions, transition metal ions such as Zn^{II} or Co^{II} can bind two Mebip ligands and thus act as a chain extender to generate linear (or macrocyclic) polymers (or oligomers) of **16** (see Figure 14a). Lanthanide ions (e.g., La^{III}, Eu^{III}) can bind up to three Mebip ligands and thus potentially act as a trifunctional cross-linker. Therefore, gel properties can be tailored by manipulation of metal ion combinations and taking into account the role of counterion coordination.

Studies demonstrated that the gel properties are the result of a phase separation and crystallization process, which produces a dispersion of spherulite-like globular colloidal particles. The interactions between these particles, which may reflect electrostatic forces and metal ion-ligand binding, in addition to the usual van der Waals interactions, give rise to the formation of a network structure. The disruption of this network by mechanical shear, and its facile re-formation when shear is removed, are the origin of the pronounced thixotropic behavior of the gels. Further studies[56] have shown that a similar phase-separated gel morphology (Figure 14b) can also be obtained, and to a certain extent controlled, if a mixed solvent system consisting of a good solvent (DMSO) with a nonsolvent (water) is used. Increase of DMSO content leads to a reduction in the particle size, refractive index contrast, and degree of crystallinity, accompanied by an increase in sol concentration and gel transparency (Figure 14c). These changes in structure and morphology are accompanied by an increase in the shear storage modulus of the gel up to a maximum value (as the particles get smaller and surface area gets larger), beyond which the modulus decreases (Figure 14d), presumably a consequence of reduced gel fraction as the solvation ability of the solvent is improved. Thus, by tailoring the solvent composition, it is possible to produce highly transparent gels, which are very strong but which are also highly mechano-responsive; i.e., they exhibit pronounced yielding and thixotropic behavior.

Nanostructured Interfacial Assemblies

Utilizing dynamic assemblies to generate useful nanoarchitectures is another active area of research. Such architectural assemblies can occur in solution (e.g., Figure 8), in the solid state (e.g., Figure 12), or at an interface. The interfacial assembly of main-chain supramolecular polymers is an interesting subclass of supramolecular polymerizations as they arrange spontaneously, given favorable conditions, and can thus be considered as a key tool with which bottom-up nanostructures can be obtained.[57,58]

At the simplest level, as far as molecular design is concerned, alkanes are known to epitaxially assemble on graphite surfaces employing van der Waals forces to direct ordered constructions.[59] Addition of a supramolecular headgroup onto alkyl chains allows for a further degree of ordering in the form of head-to-head/tail-to-tail assembly.[60] One example of a supramolecular head/alkyl tail arrangement in noncovalent surface assembly comes from Bernasek and co-workers.[61] Deposition of 5-octadecyloxyisophthalic acid (**17**, Figure 15a) from phenyloctane solution onto highly ordered pyrolytic graphite (HOPG) leads to a self-assembled monolayer that spontaneously forms a banded pattern with 37−38 Å spacing between the bands as observed by high-resolution STM images (Figure 15b). The researchers propose that the bands are constructed from the interdigitation of the alkyl tails as the molecules adsorb onto the HOPG. It is postulated that the bands are stabilized by a combination of hydrogen bonding between the carboxylic acid moieties and the alkyl chain−chain van der Waals forces. Simply changing the solvent from phenyloctane to octanoic acid (which can hydrogen bond to **17**) rearranges the assembly into smaller bands with regular gaps (of 8.5 Å × 13.5 Å × 1.8 Å) in the pattern.

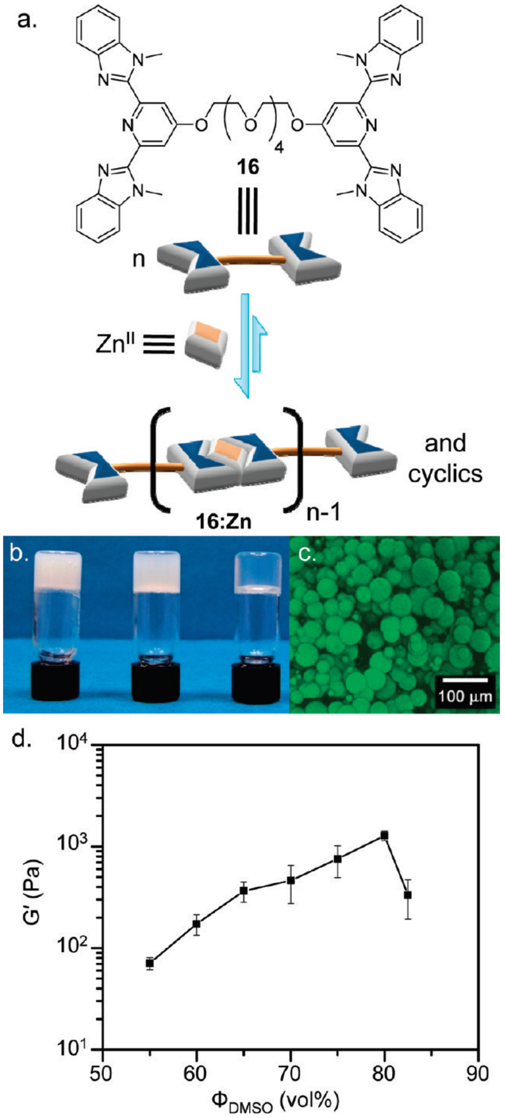


Figure 14. Schematic representation of the formation of metallo-supramolecular polymeric aggregates (**16·Zn**) using ditopic ligand end-capped monomers **16** with $Zn(ClO_4)_2$ that can (b) form gels in mixed solvents from left to right, DMSO/water in ratios of 60/40, 70/30, and 80/20 (v/v). (c) Laser scanning confocal microscopy (LSCM) *z*-projection image of the **16·Zn** gel formed in 60/40 (v/v) DMSO/water mixture and (d) the storage modulus values, taken from the frequency sweep measurements at a frequency of 1 Hz, of various **16·Zn** DMSO/water gels. The shear strain applied is 0.2%, and the gel concentration is 50 mg/mL. Pictures and data taken from ref 56.

Figure 15c shows the narrower 32−34 Å bands along with the proposed packing pattern of alternating **17** with octanoic acid. Conceptually, the size of the gaps could be tailored by using longer chain acids, and this effect was reported, though the octanoic acid coassembly proved to be the most stable assembly. Again, hydrogen-bonding and interchain van der Waals interactions between alkyl tails are proposed to stabilize the assembly. This system highlights how the addition of simple noncovalent interactions into a monomer adsorbate can have a dramatic effect on the nature of the interfacial assemblies.

An interesting demonstration of the nature of the growth of similar types of amphiphilic assemblies was recently reported by Rowan, Marchant, and co-workers.[62] Deposition of dilute solutions of the monotopic monomer **18** (a guanine moiety with a hydrophobic tail, Figure 16a) onto HOPG from H_2O/DMSO (49:1) revealed an anisotropic growth of the two-dimensional

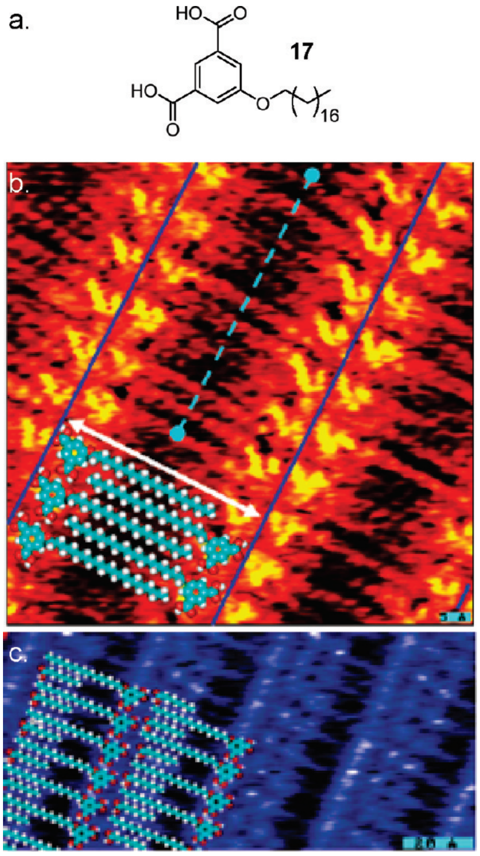


Figure 15. (a) Chemical structure of 5-octadecyloxyisophthalic acid (**17**), (b) high-resolution STM image of **17** on HOPG with proposed molecular orientation overlay, and (c) high-resolution STM image of **17** with octanoic acid, forming regularly spaced voids. Figures taken from ref 61.

assembly, as monitored in real time by fluid tapping mode AFM (Figure 16b−d). Each of these needlelike assemblies is comprised of 5.4 nm bands (Figure 16e). Molecular modeling suggests that the assembly occurs through a double-stranded hydrogen-bonding guanine assembly (Figure 16f,g). The modeling further suggests that while the growth of the assembly occurs along the *y*-axis (as defined in Figure 16f,g) with the aid of hydrogen bonding, growth in the *x*-axis direction would be aided by the weaker van der Waals interactions. Thus, it was proposed that, after adsorption onto the graphite surface from solution, the monomer preferentially adds onto the assembly along the *y*-axis with the aid of hydrogen bonding, resulting in the observed initial needlelike assemblies. Growth along the *x*-axis does occur albeit at a slower rate, and given enough time and material complete monolayers assemblies are achieved.

The same group has also studied the assembly of ditopic guanine-based monomers **19a**−**19d** (Figure 17a) and has shown that these compounds also form molecular sized banding patterns at the HOPG/water interface.[63] The size of the banding pattern can be controlled by the length of the alkyl chain core, from 3.2 to 4.8 nm, and the core alkyl chain length (*R*) increases from 8 to 18 carbons. The group went on to shown that similar banding patterns (Figure 17b) could be obtained even if a side group is attached to the core, as is the case for **19e**, which would presumably result in the surface being decorated with short triethylene glycol units (Figure 17c). To demonstrate the presence of these units on the surface, the material was incubated with platelet-rich plasma, and the percentage of platelets adhered to the surface was quantified. Surfaces with poly(ethylene glycol) units attached are known to hinder nonspecific protein adsorption and therefore the formation of platelets.[64] In this case the HOPG coated with the triethylene glycol containing monomer **19e** shows dramatically less platelet coverage compared to the more hydrophobic bare HOPG or HOPG coated with **19c** (approximately 21%, 35%, and 38% platelet coverage, respectively). This shows that the formation of main-chain supramolecular polymers on a surface can be used as a template to facilely position functional groups on a surface at the nanoscale and that such displayed groups can exhibit a function.

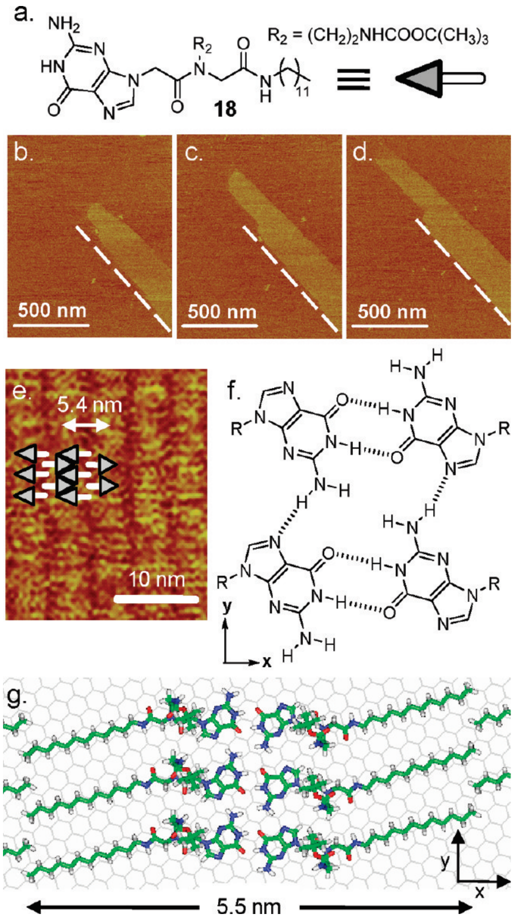


Figure 16. (a) Structure of monotopic monomer **18**. Real-time AFM images of the growth of **18** on HOPG from aqueous solutions after (b) $t = 0$ min, (c) $t = 5$ min, and (d) $t = 10$ min. (e) AFM image of the resulting assembled banding pattern of **18** and schematic overlay of proposed head-to-head/tail-to-tail nanoassembly and (f) the proposed hydrogen-bonding guanine motif and (g) the molecular modeling of **18** on HOPG. Figure adapted from ref 62.

More complex surface assemblies than simple tapes can be constructed by utilizing many of the options available to supramolecular chemists.[65] For example, Champness, Beton, and coworkers[66] reported the assembly of a B−B plus A_3 comonomer system. After stepwise vapor deposition under ultrahigh vacuum of perylene tetracarboxylic diimide (**20**) and melamine (**21**) (Figure 18a) onto silver-terminated silicon, they found that upon annealing these monomers assembled into a honeycomb-like structure on the surface (Figure 18b). Here **21** is the A_3 monomer that acts as the vertices of the hexagonal assembly with the ditopic **20** acting as the edges and the formation of the coassembly being driven through the complementary triple hydrogen-bonding sites on both molecules (Figure 18a). These structures produced nanosized pores (or cavities) that were large and stable enough to further organize seven C_{60} guest molecules into heptameric clusters (Figure 18b), further highlighting how much control can be attained on surface nanoassemblies through careful

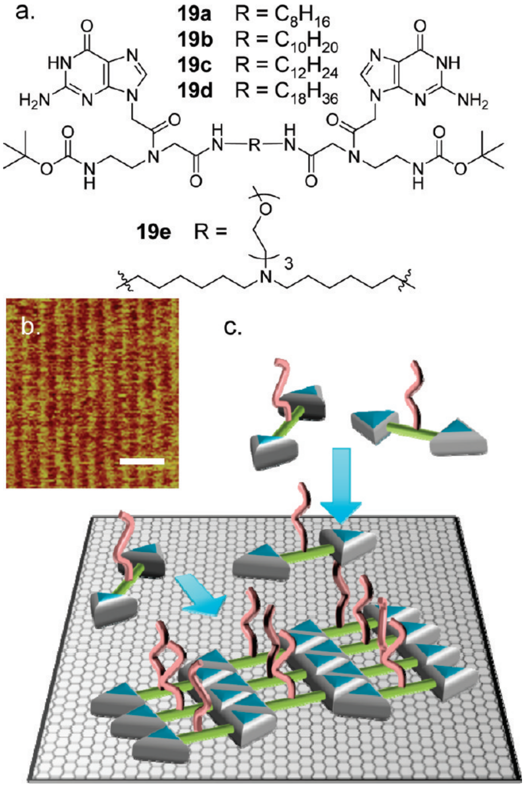


Figure 17. (a) Ditopic monomers (**19a**−**19e**) used to form self-assembled banding structures on HOPG, (b) AFM image of the assembly of **19e** (scale bar 10 nm),[63a] and (c) a schematic of **19e**'s proposed assembly that results in the supramolecular functionalization of the surface.

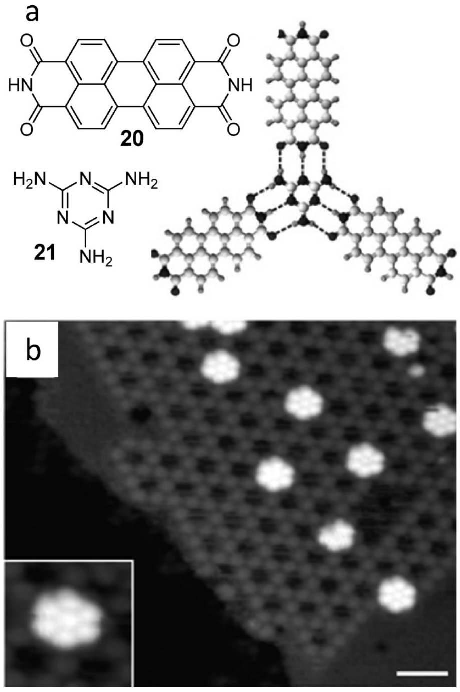


Figure 18. Structures of the two monomers **20** and **21** and the proposed hydrogen-bonding scheme that results in a honeycomb lattice and (b) the STM image of honeycomb structure with C_{60} heptamers appearing as brighter spots within; scale bar 5 nm. Inset: enlarged C_{60} heptameric aggregate. Figure adapted from ref 66.

supramolecular design and processing conditions. The further development, understanding, and utilization of such tailored assemblies will prove paramount to the advancement of nanotechnology as length scales shrink beyond the effectiveness of conventional methods for controlling architectures.

Conclusion and Outlook

Bestowed with the key property of reversibility, main-chain supramolecular polymers have generated a tremendous amount of research interest aimed at exploring the new matrix of properties that such polymers offer. This perspective has only been able to highlight a few of examples and concepts (particularly as they relate to stimuli-responsive materials and nanoassemblies) that have helped this field to grow over the past 30 years or so. However, there is much still to know and explore in this field with plenty of growth potential in all kinds of areas. For example, the reversible nature of these polymeric assemblies yields materials with stimuli-sensitive mechanical properties that hold promise as rehealable materials,[67] "reworkable" adhesives, or recyclable plastics. The growing area of low molecular weight[68] or polymeric supramolecular gels is one that was only briefly touched upon in this perspective but is a field that holds promise for a number of arenas ranging from viscosity modifiers to easy-to-tailor biomaterials.[69] Supramolecular polymers are also being investigated to access easy-to-process opto-electronic materials that can show enhanced mechanical[70] or easy-to-tune optical properties.[71] No doubt as a better understanding of these systems is obtained, through both experimental and theoretical studies, more innovative new materials will be developed and new applications sought. As these advances are made, the concepts of supramolecular chemistry and materials will find their way into everyday life to enable technologies and processes not previously possible. Given such promise, supramolecular polymers perhaps will not replace traditional polymers, but will exist as their own separate and important class of engineered materials.

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