

Supramolecular Polymers

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I. Introduction

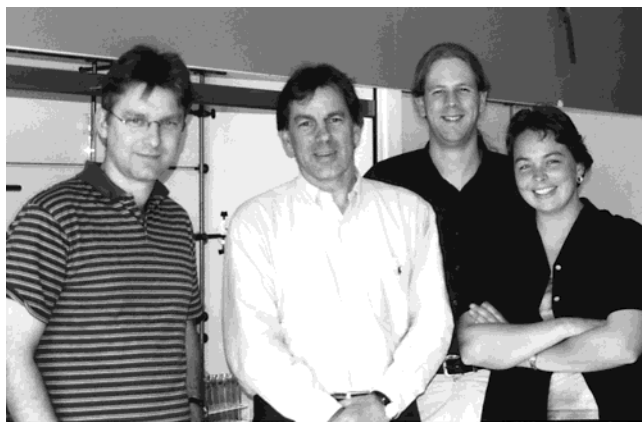
With the introduction of supramolecular polymers, which are polymers based on monomeric units held together with directional and reversible secondary interactions, the playground for polymer scientists has broadened and is not restricted to macromolecular species, in which the repetition of monomeric units is mainly governed by covalent bonding. The importance of supramolecular interactions within polymer science is beyond discussion and dates back to the first synthesis of synthetic polymers; the

materials properties of, e.g., nylons, are mainly the result of cooperative hydrogen bonding. More recently, many exciting examples of programmed structure formation of polymeric architectures based on the combination of a variety of secondary supramolecular interactions have been disclosed.

When the covalent bonds that hold together the monomeric units in a macromolecule are replaced by highly directional noncovalent interactions (Figure 1), supramolecular polymers are obtained. In recent years, a large number of concepts have been disclosed that make use of these noncovalent interactions. Although most of the structures disclosed keep their polymeric properties in solution, it was only after the careful design of multiple-hydrogen-bonded supramolecular polymers that systems were obtained that show true polymer materials properties, both in solution and in the solid state. Polymers based on this concept hold promise as a unique class of novel materials because they combine many of the attractive features of conventional polymers with properties that result from the reversibility of the bonds between monomeric units. Architectural and dynamic parameters that determine polymer properties, such as degree of polymerization, lifetime of the chain, and its conformation, are a function of the strength of the noncovalent interaction, which can reversibly be adjusted. This results in materials that are able to respond to external stimuli in a way that is not possible for traditional macromolecules. These aspects of supramolecular polymers have led to a recent surge in attention for this promising class of compounds^{1–3} and have stimulated us to bring together materials science and supramolecular chemistry.⁴ On the other hand, it is obvious that a large number of important properties of polymers require the covalent and irreversible bonding of the repeating units in the main chain. For applications in which all of these properties are important, supramolecular polymers are not the perfect choice. However, the opportunity to combine macromolecules and concepts derived from supramolecular polymers also has an enormous potential to alter the properties of polymers in a controlled way.

II. The Term Supramolecular Polymers

Interest in supramolecular polymers has been stimulated to a great extent by the impressive progress made in supramolecular chemistry in general,^{5–8} and in the field of synthetic self-assembling molecules in particular. The field in which



Luc Brunsveld (second from right) received his Ph.D. in Supramolecular Chemistry at the Eindhoven University of Technology in 2001 with professor E. W. Meijer. The Ph.D. research was focused on supramolecular architectures in water and a small part of that has been performed in the group of professor J. S. Moore at the University of Illinois, Urbana—Champaign. He did his undergraduate research in the group of professor E. W. Meijer on supramolecular hydrogen-bonded polymers. His research interests are in the field of supramolecular architectures and chirality. Currently he is working as a postdoctoral fellow in the group of professor Waldmann at the MPI in Dortmund, Germany.

Brigitte J. B. Folmer (right) received her B.A. degree in chemistry from the University of Nijmegen in 1996, where she did her graduation work on host–guest chemistry in the group of professor R. J. M. Nolte. In 2000 she received her Ph.D. degree from the University of Technology in Eindhoven with professor E. W. Meijer. Her thesis was focused on the properties of supramolecular polymers based on hydrogen bonding. Currently she is working at Organon N. V. (AkzoNobel) in Oss, The Netherlands. Her research interests include organic synthesis and supramolecular chemistry and particularly the role of noncovalent interactions in receptor–ligand complexes and supramolecular materials.

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Rint P. Sijbesma (left) did his graduate research with professor Roeland Nolte at the University of Nijmegen; the focus was on synthetic receptor molecules. From 1992 to 1993 he worked as a postdoctoral research assistant with professor Fred Wudl (University of California, Santa Barbara) on the synthesis of water-soluble C_{60} -derivatives. In 1993 he took his present position as assistant professor in the laboratories of professor E. W. Meijer, where he is working in the field of supramolecular polymer chemistry.

supramolecular chemistry and polymer science meet has developed into a vast area of research, ranging from the study of interacting biomacromolecules, such as DNA and proteins, to the self-assembly of large synthetic molecules into well-defined architectures. Examples of the latter include the formation of PMMA stereocomplexes, highly organized block-copolymer architectures, and self-assembled polymer architectures inspired by the structure of tobacco mosaic virus (TMV).⁹ Noncovalent interactions have also been employed to fold macromolecules (aptly

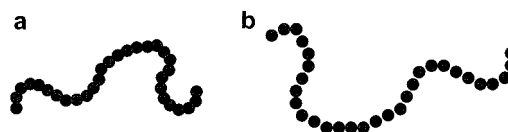


Figure 1. Schematic representation of a covalent polymer (a); and a supramolecular polymer (b).

named “foldamers”)¹⁰ into well-defined conformations. These examples of using secondary interactions in and between synthetic macromolecules typify the potential of a supramolecular approach to highly organized, functional materials.

Partly influenced by our own research interests, the focus in this review is on the role of specific, noncovalent interactions such as hydrogen bonding, metal coordination, and π – π (or arene–arene) interactions to form so-called supramolecular polymers. The high directionality of these interactions inherently stresses the one-dimensional nature of these polymers. It is instructive to notice that from this point of view, supramolecular polymers and crystalline compounds are at opposite ends of the spectrum of molecular materials. In molecular crystals, it is difficult to define a dominant direction of the interactions – crystals are fundamentally 3-dimensional – and even when interactions are stronger in one direction than in others, all specific aggregation is lost when these materials are heated or dissolved. Supramolecular polymers, on the other hand, are 1-dimensional in nature, and in melts or (dilute) solutions of these materials distinguishable polymeric entities continue to exist. A fascinating intermediate class of materials consists of compounds that form polymers in the liquid crystalline state. Here, cooperativity between a relatively weak secondary interaction and excluded volume interactions (which are entropic in nature) leads to a significant degree of polymerization.¹¹ However, in the isotropic melt or in solution, most of the polymeric properties are lost. Because hydrogen-bonded liquid crystals have played an important role in developing the concept of supramolecular polymers, they will be covered in some detail in this review. Polymers that are held together by topological constraints, such as polycatenanes and polyrotaxanes, will not be treated in this review.¹²

Taking everything into account, we like to propose the following definition for supramolecular polymers: *Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solutions, as well as in the bulk. The monomeric units of the supramolecular polymers themselves do not possess a repetition of chemical fragments. The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics.* In the past the term “living polymers” has been used for this type of polymers. However, to exclude confusion with the important field of living polymerizations, we prefer to use the term supramolecular polymers. With this definition, the term supramolecular polymer is rather restricted and not

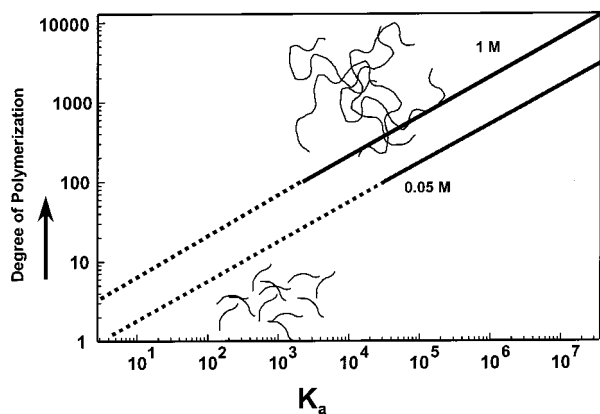


Figure 2. Theoretical relationship between the association constant K_a and DP, using a simple isodesmic association function, or “multistage open association” model.

used for telechelic macromolecules reversibly bound together by specific supramolecular interactions. However, modified telechelics are included in this review because many issues in the field are important for associating telechelics as well.

III. General Aspects of Supramolecular Polymers

It is useful to review some of the general aspects of the supramolecular approach, taking into account the limitations of our definition of supramolecular polymers. Using a directional complementary couple (A–B) or a self-complementary unit (A–A), it is possible to form all known structures of polymers, including linear homo- and copolymers, cross-linked networks, and even (hyper)branched structures in the case of complementary couples.¹³ In supramolecular polymers, which are formed by the reversible association of bifunctional monomers, the average degree of polymerization (DP) is determined by the strength of the end group interaction.¹⁴ The degree of polymerization is obviously dependent on the concentration of the solution and the association constant, and a theoretical relationship is given in Figure 2.

To obtain polymers with a high molecular weight, a high association constant between the repeating units is a prerequisite. In analogy with covalent condensation polymers, the chain length of supramolecular polymers can be tuned by the addition of monofunctional “chain stoppers”.¹⁵ This also implies that impurities will have a strong influence on the maximal DP, because it is easy to have a small fraction of monofunctional impurity in the synthesis of the bifunctional monomer. Hence, as in traditional polymer synthesis, the purification of the monomers is extremely important to obtain high molecular weights.

In another approach, supramolecular polymers can be formed by planar structures that have the possibility to assemble on both sides of the plane. Here, one structural element is responsible for the formation of the polymer, and chain stoppers are difficult to design. Hence, the DP is completely governed by the association constant and the concentration. As a result of the structural motive, these supramolecular polymers are rather stiff and resemble rodlike poly-

mers, with interesting architectural properties but without significant materials properties in the bulk.

In a third approach, supramolecular polymers are based on the reversibility of metal-coordination bonding. These polymers are the closest analogues to conventional macromolecules, because most of the polymers disclosed make use of strong bonding,¹⁶ in which the reversibility can be tuned by chemical means only. However, appropriate choice of the metal ion can give rise to bonding that resembles that of the other two approaches. The DP of the polymers in the case of the coordination polymers is similar to that of the condensation polymers, and achieving exact stoichiometry is of distinct importance here.

True supramolecular polymers are reversible aggregates that can break and recombine on experimental time scales. It is this feature that has been investigated in detail by Cates in a physical model, predicting stress relaxation and other viscoelastic properties of entangled “living polymers” as a function of the interaction strength of the monomer end groups.^{17–19} Although this model was made for cylindrical micelles, it is shown by the work on ureidopyrimidone-based supramolecular polymers that the model also describes in detail the viscosity behavior of reversible supramolecular polymers. Many of the materials properties of supramolecular polymers are those well-known for traditional polymers, although the reversibility will lead to an unconventional temperature dependence of the materials’ properties.

IV. Supramolecular Polymers Based on Hydrogen Bonding

Although hydrogen bonds between neutral organic molecules are not among the strongest noncovalent interactions, they hold a prominent place in supramolecular chemistry because of their directionality and versatility.^{20–22} The relationship between the degree of polymerization and the strength of the noncovalent interaction between monomers in a supramolecular polymer (see Figure 2) implies that cooperativity is required to obtain significant degrees of polymerization. Hence, either multiple-hydrogen bonds must be used or hydrogen bonds should be supported by additional forces, like excluded volume interactions. Examples of both approaches to hydrogen-bonded supramolecular polymers will be discussed.²³

A. Strength of Hydrogen Bonds

Combining several hydrogen bonds in a functional unit is a valuable tool for increasing the strength of this interaction, and employing a particular arrangement of the hydrogen bonding sites enhances its specificity. The strength of single hydrogen bonds basically depends on the nature of donor and acceptor, although it is influenced to a large extent by the solvent. Association strength between multiple hydrogen-bonding units obviously depends on the same factors, as well as on the number of hydrogen bonds. It has also been shown that the particular arrange-

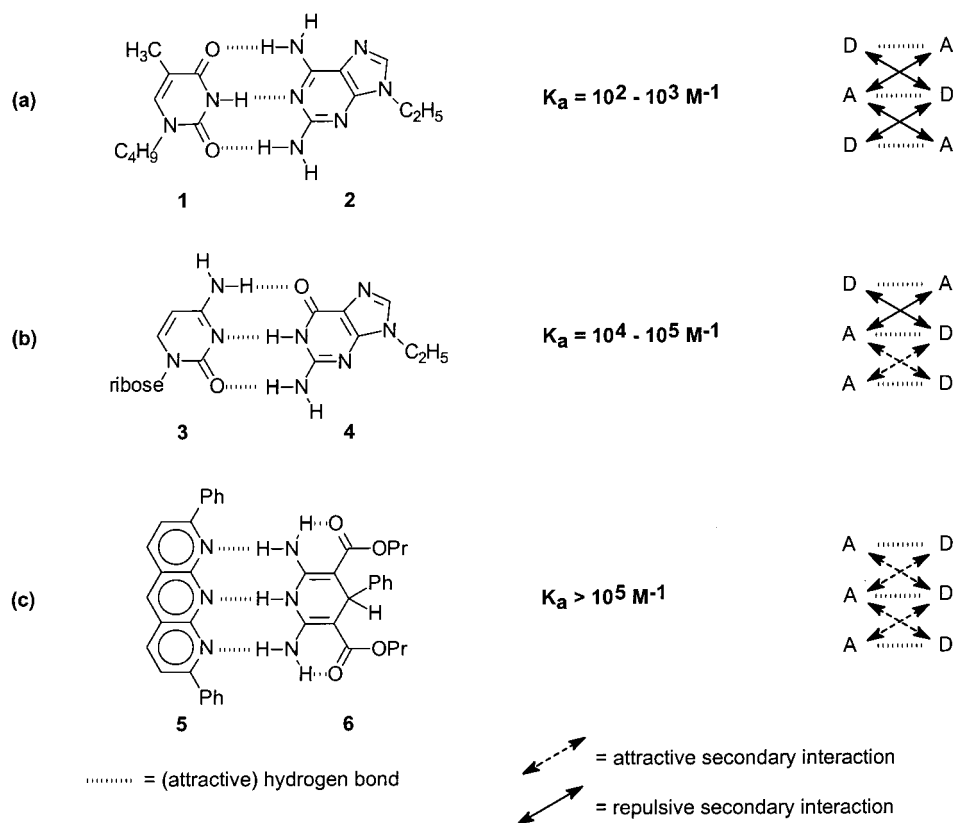


Figure 3. Stability of complexes with different hydrogen-bonding motifs.

ment of neighboring donor and acceptor sites is an additional factor which significantly affects the strength of the complexation. This phenomenon was first recognized for the association of linear arrays of 3 hydrogen-bonding sites (Figure 3); whereas complexes between the common ADA–DAD (1–2) motif exhibit an association constant of around 10^2 M^{-1} in chloroform, this value is around 10^4 M^{-1} in complexes with a DAA–DDA (3–4) motif, while AAA and DDD arrays (5–6) exhibit association constants exceeding 10^5 M^{-1} . Detailed calculations by Jorgenson^{24,25} showed that this effect is due to differences in secondary interactions between these motifs. In the complexes, diagonally opposed sites repel each other electrostatically when they are of the same kind (both donor or both acceptor), whereas disparate sites attract each other. In the DDD–AAA motif the number of attractive secondary interactions is maximized, and in the ADA–DAD motif the number of repulsive interactions is at its largest.

Very stable complexes can be obtained when quadruple hydrogen-bonding units are employed.^{26–30} Aspects of multiple hydrogen-bonding units that are of special importance with respect to application in supramolecular polymers are the self-complementarity of DADA and DDAA arrays and the possibility of tautomerism. The latter may lead to loss of complexation when complementarity is lost, or when a DDAA array tautomerizes to a DADA array with a higher number of repulsive secondary interactions. We have reported on self-complementary quadruple H-bonding units based on mono-ureido derivatives of diamino-triazines²⁹ (DADA-array) with a dimerization constant of $K_{\text{dim}} = 2 \times 10^4 \text{ M}^{-1}$ and hydrogen-

bonding units based on 2-ureido-4[1H]-pyrimidinones (DDAA), which dimerize in chloroform with an association constant of $K_{\text{dim}} = 6 \times 10^7 \text{ M}^{-1}$.^{30,31} The supramolecular polymers that were developed using these hydrogen-bonding units will be discussed in detail below. Zimmermann and co-workers have reported a very stable self-complementary quadruple hydrogen-bonding unit (7), depicted in Figure 4, in which all tautomers can dimerize via quadruple hydrogen bonds.

There is ample opportunity for developing new multiple hydrogen-bonding units for use in supramolecular polymers with novel, attractive features, such as ease of synthesis, insensitivity to tautomerization,²⁸ and stronger association by using arrays of 6 bonds³² or 8 hydrogen bonds.³³ The use of heteroaromatic compounds as multiple hydrogen-bonding units for self-assembly has recently been reviewed.³⁴

Application of hydrogen-bonding units as associating end-groups in difunctional or multifunctional molecules results in the formation of supramolecular polymers with varying degrees of polymerization (DP). The early examples of hydrogen-bonded supramolecular polymers rely on units, which associate using single, double, or triple hydrogen bonds that all have association constants below 10^3 M^{-1} . In isotropic solution, the DP of these polymers is expected to be low. In the liquid crystalline state, however, the interactions are stabilized by excluded volume interactions, and the DP is much higher. Examples of linear supramolecular polymers based on weak hydrogen-bonding interactions assisted by liquid crystallinity or phase separation will be treated below, followed by a discussion of supramolecular

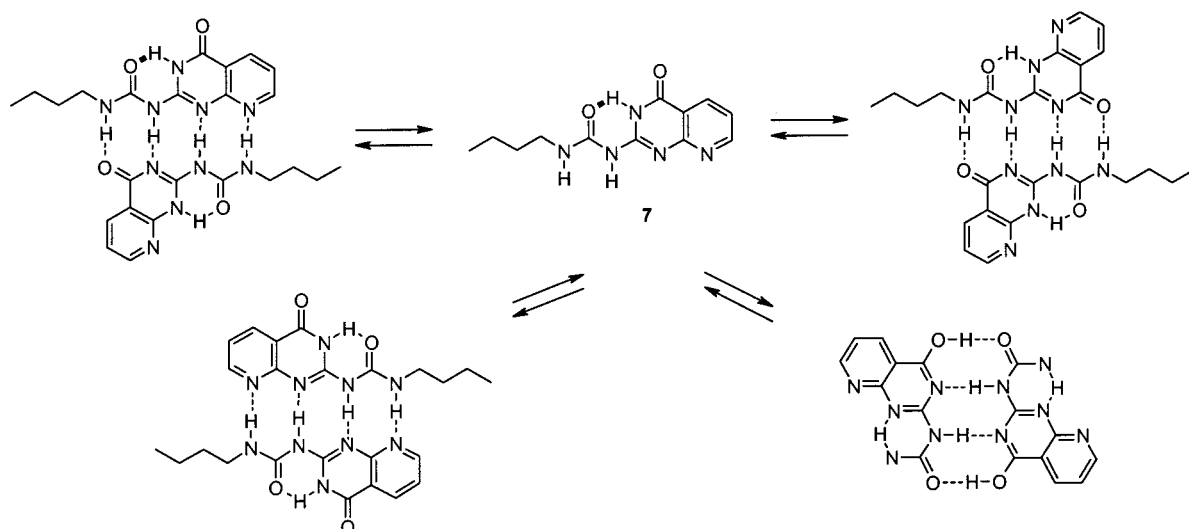


Figure 4. Hydrogen-bonding unit **7** that dimerizes via quadruple hydrogen bonding without regard to tautomeric form.

polymers based on strong hydrogen-bond interactions that persist in the isotropic state (melt or solution).

B. Hydrogen Bonding Enforced by Liquid Crystallinity

The first hydrogen-bonded supramolecular polymers all showed liquid crystallinity, although the separate components making up these polymers displayed a narrow liquid crystalline regime or no liquid crystallinity at all. The liquid crystalline phase in the supramolecular polymer is stabilized by the increased aspect ratio of aggregates compared to the constituent molecules. There is a strong cooperativity between association and the induction of the liquid crystalline phase, because anisotropy in the liquid crystal strongly enhances the degree of polymerization of the hydrogen-bonded molecules.³⁵ Liquid crystalline supramolecular polymers are unique in the respect that they combine the potential to exhibit the electrooptical properties associated with low-molar-mass liquid crystals with the benefit of the good mechanical properties of conventional polymers.³⁶ Odijk,^{37,38} van der Schoot,³⁹ and Ciferri⁴⁰ developed a theoretical basis for the relation between chain growth and orientation in supramolecular liquid crystals.

The group of Lehn is recognized to be the first to develop a supramolecular main-chain polymer. By triple hydrogen bonding between difunctional diaminiopyridines (**8**) and difunctional uracil (**9**) derivatives (Figure 5) supramolecular polymer chains were formed (**10**).^{41,42} The 1:1 mixture of **8** and **9** exhibits liquid crystallinity over a broad temperature window, whereas, in contrast, the pure compounds are solids which melt in an isotropic liquid without displaying a liquid crystalline phase. Because of the chirality of the tartaric acid spacer used, the fibers observed by electron microscopy showed biased helicity.⁴³ Lehn and co-workers expanded the scope of supramolecular polymers by the development of rigid rod polymers (**11**, Figure 5).^{44,45} In these polymers, a rigid 9,10-dialkoxyanthracene core connects the hydrogen-

bonded groups via an imide group. Because of the increased molecular rigidity, the system is not thermotropic liquid crystalline, but a lyotropic liquid crystalline phase is observed in apolar solvents, that is birefringent and highly viscous.

A number of supramolecular liquid crystalline polymers based on a single hydrogen bond have been reported. Incorporation of single hydrogen-bonding units is synthetically more straightforward than those with triple hydrogen bonds, and, particularly, the single hydrogen bond between a pyridyl unit and carboxylic acids has been utilized frequently in supramolecular liquid crystalline polymers (LCP's).^{46–50} The complexation between a pyridyl unit and a carboxylic acid is stronger than carboxylic acid dimerization; a K_a value of approximately 500 M^{-1} was estimated for the pyridyl/carboxylic acid complex.⁴⁷ Kato and Fréchet have described a variety of self-assembled side-chain liquid crystalline polymers (SLCPs), with various backbones.^{48,49} Polyacrylates and polysiloxanes functionalized with pendant benzoic acids display stable mesophases upon self-assembly with stilbazoles. The reverse principle has been employed for the formation of supramolecular liquid crystalline polyurethanes.⁵⁰ Furthermore, the stability of the induced mesophase has been enlarged by employing the double hydrogen bond between benzoic acids in the polymer main-chain and 2-(acylamino)pyridines.^{51,52}

Utilization of the single hydrogen bond between pyridine and benzoic acids in SLCP's has been a source of inspiration for other groups in the development of main-chain supramolecular polymers based on diacids and dipyridines.^{53–56} Supramolecular rod-coil polymers have been developed by assembly of 4,4'-bipyridines and telechelic polypropylene oxide with benzoic acid end-groups, which show highly ordered liquid crystalline phases.⁵⁷ The use of tartaric acid derivatives in combination with bipyridine units resulted in the formation of hydrogen-bonded, chiral main-chain LCP's, as has been shown by circular dichroism measurements, optical microscopy, and X-ray data.^{58,59}

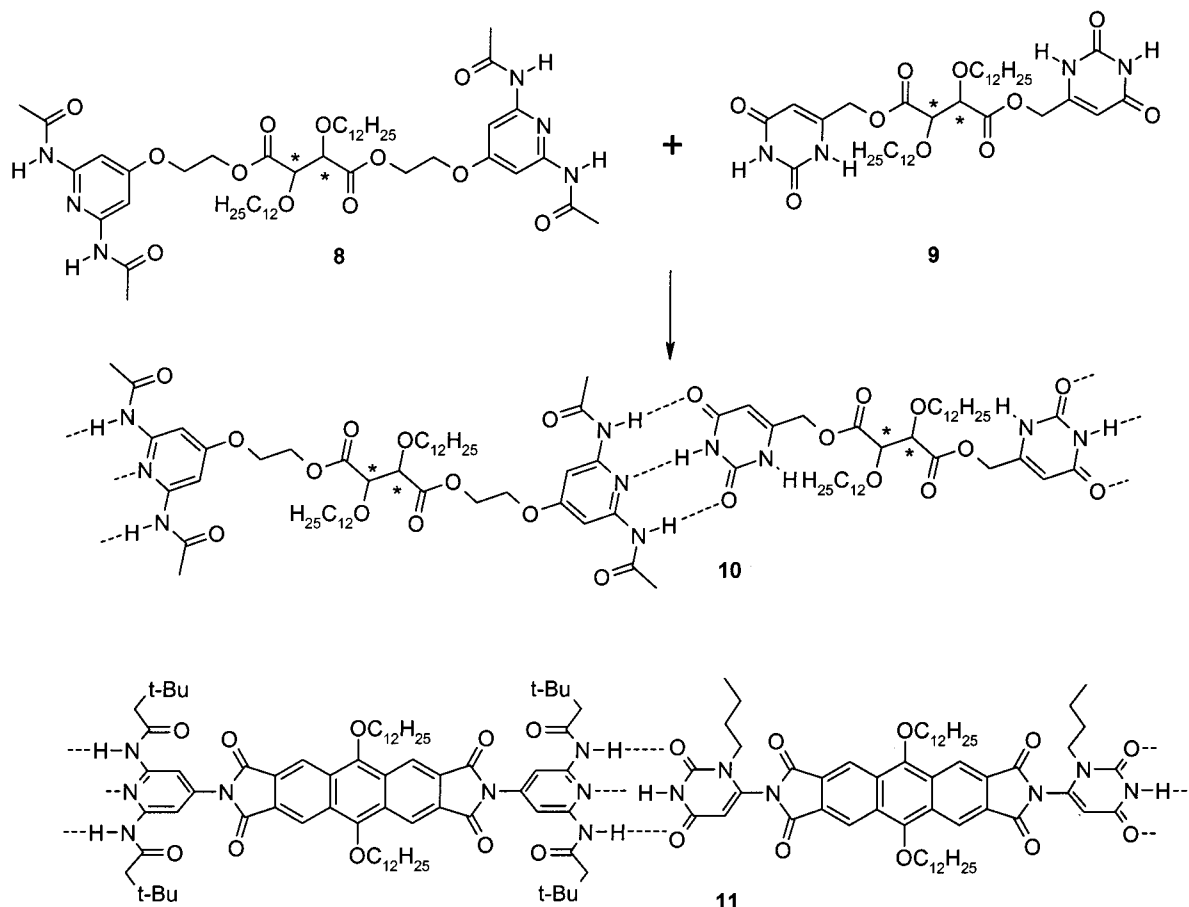


Figure 5. Liquid crystalline supramolecular polymers developed by Lehn, based on triple hydrogen bonds: from chiral, tartaric acid based monomers (**10**) and from rigid monomers (**11**).

A columnar mesophase has been used by the group of Percec for the creation of hydrogen-bonded supramolecular polymers.^{60,61} The phase separation of the apolar side groups of substituted benzamides with the core of the molecule accounts for the self-assembly into a cylindrical structure in which hydrogen bonding acting along the columnar axis occurs and stabilizes the column.

Next to side-chain LCPs and main-chain LCPs, supramolecular networks were obtained by complexation of bipyridines with polyacrylates containing pendant benzoic acid groups. In a related approach, Kato and Fréchet have studied supramolecular networks based on low-molecular-weight components, in which a trifunctional benzoic acid derivative was combined with a difunctional pyridine derivative.⁶² The hierarchy of the LC-phase that was formed turned out to be dependent on the flexibility of the trifunctional compound used.

Although chain extension based on single hydrogen bonding is observed, supramolecular materials based on this interaction, in most aspects, resemble small molecules more than they resemble polymers. Only the triple hydrogen-bonded supramolecular polymers reported by Lehn show some typical polymer properties, such as the ability to draw fibers from the melt. By using multifunctional low-molecular-weight building blocks, Griffin was able to obtain materials that exhibited polymer-like properties.⁶³

Hydrogen bonding between pyridine units in a tetrafunctional compound (**12**) and benzoic acid units in difunctional compounds (**13**, Figure 6), resulted in the formation of reversible ladder-like polymers (**14**) or networks (**15**). These materials are liquid crystalline, and the large drop in material properties above the isotropisation temperature demonstrates that, also here, the interplay between association and liquid crystallinity is instrumental in the process of polymerization.⁶³ DSC studies on these networks reveal a memory effect, resulting in a consistent decrease of crystallinity as the time the material is in the isotropic state increases.⁶⁴

C. Hydrogen Bonding Enforced by Phase Separation

The methodology of increasing the strength of a relatively weak hydrogen-bond interaction by (crystalline) domain formation is frequently encountered in chain extension of conventional polymers, and is in principle analogous to the enforcement of association in the liquid crystalline phase. Lillya et al. has shown that by end-capping of poly-THF with benzoic acid functionalities, the material properties improve significantly due to the formation of large crystalline domains of the hydrogen-bonded units.⁶⁵ Furthermore, end capping of poly(dimethylsiloxane)s with benzoic acid groups has been reported to result in a change in polymer properties upon functionalization. However, the change in properties seems to be less

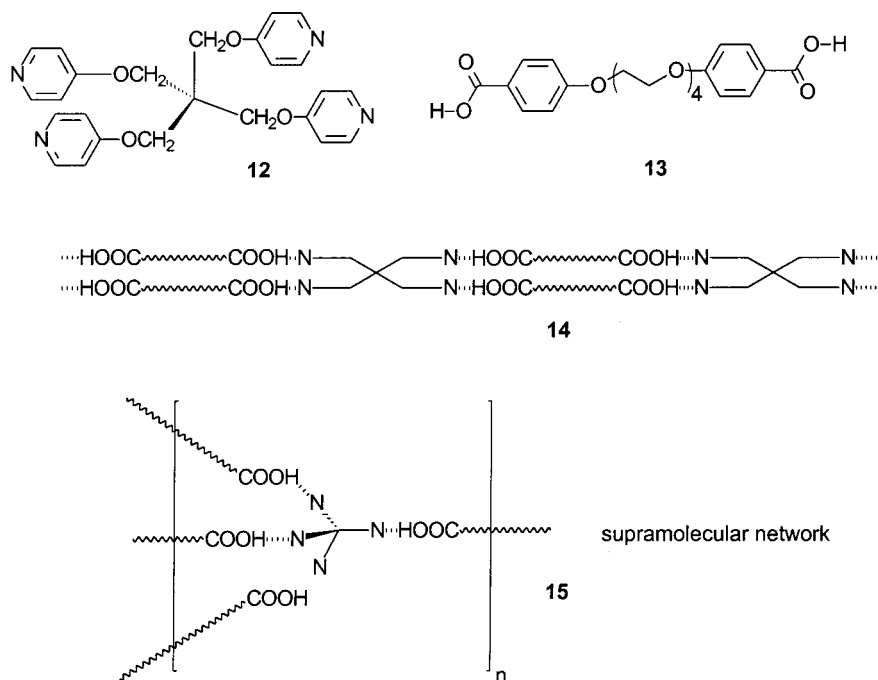


Figure 6. Formation of a linear ladder-type supramolecular polymer (**14**) or a hydrogen-bonded network (**15**) based on the single hydrogen bond between a pyridine unit and a benzoic acid unit.

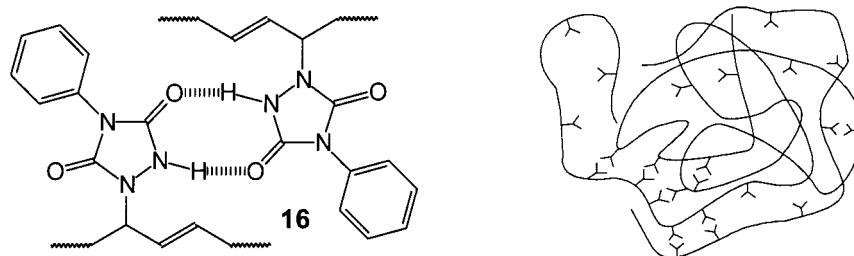


Figure 7. Formation of a supramolecular network by hydrogen bonding between phenylurazole units and subsequent formation of ordered clusters.

remarkable than the results obtained with poly-THF.⁶⁶ On the basis of detailed FTIR spectroscopy and viscosimetry studies, a quantitative model for the chain length and weight distribution of the functionalized polysiloxane in solution was described by Bouteiller et al.⁶⁷ These associative polymers with hydrogen-bonded groups, either telechelic or in the side-chains, are of considerable interest for numerous applications, such as rheology modifiers, adhesives, adsorbents, coatings, surfactants, and stabilizers, because of the reversibility of interactions in the chain and between chains.⁶⁸ Particularly, Stadler made an impressive contribution to this field by studying the properties of polybutadienes functionalized with hydrogen-bonded phenylurazole units (**16**, Figure 7).^{69–87}

Because of their reversible chain extension and the subsequent formation of small crystalline domains, the functionalized polymers exhibit properties typical for thermoplastic elastomers. At low temperatures the hydrogen-bond interaction contributes to the properties comparable to covalent interactions, whereas at high temperatures these interactions disappear and the materials exhibit flow behavior typical for a low-molecular-weight polymer. DSC,^{72,73} light and X-ray scattering,^{71,74} dynamical mechanical analy-

ses,^{75–81} dielectric spectroscopy^{82,83}, deuterium-NMR,⁸⁴ and IR spectroscopy^{85–87} were used to analyze the properties of these materials.

Although the strength of association between units, which assemble by only a single or double hydrogen bond, is low, chain extension by these synthetically accessible units is a versatile tool for gaining a significant improvement in material properties. A modest degree of polymerization in combination with physical interchain interactions by means of domain formation results in high-molecular-weight assemblies with improved material properties. Without domain formation, or when low-molecular-weight building blocks are used, a very high degree of polymerization, and consequently a high association constant, is required, as will be discussed in the following section.

D. Strong Dimerization of Multiple Hydrogen-Bonding Units

The number of supramolecular polymers based on very strong multiple hydrogen-bonded units is relatively small because of the increased synthetic efforts required for the synthesis of the monomers. Intriguing architectures such as nanotubes⁸⁸ are obtained

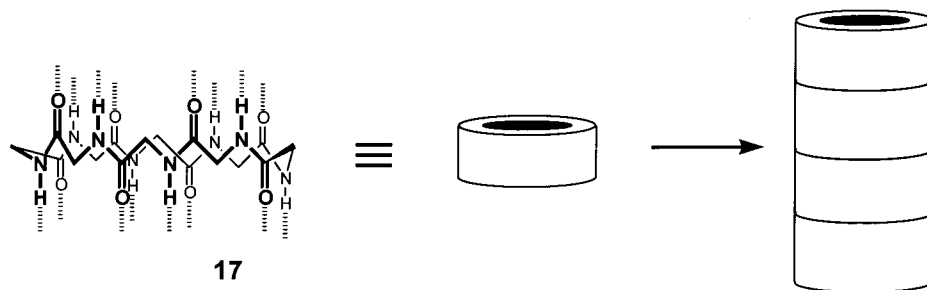


Figure 8. Formation of nanotubes based on hydrogen bonding between cyclic peptides.

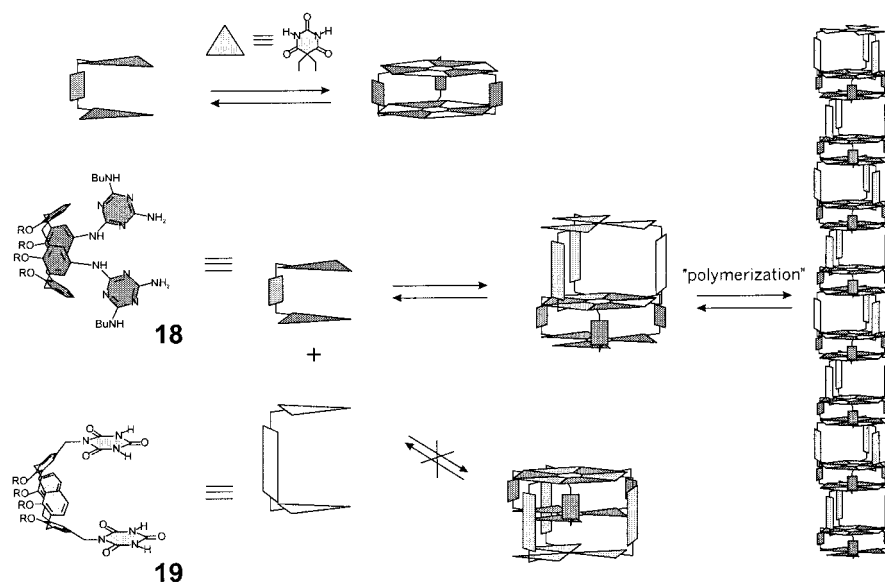


Figure 9. Nanorods based on the cyclic hydrogen-bonding motif of cyanuric acid and melamine in bifunctional calixarene derivatives **18** and **19**. (Reprinted with permission from ref 106. Copyright 1999 American Chemical Society.)

when bifunctional compounds with cyclic arrays of hydrogen-bonding sites are used. Ghadiri has studied nanotubes that self-assemble from cyclic peptides (**17**). These tubes can be considered reversible polymers because of their multiple-hydrogen bonding. On the basis of earlier work by De Santis⁸⁹ and Tomasic,⁹⁰ cyclic peptides were designed, composed of an even number of alternating d- and l-amino acids, which assemble into extended linear stacks through hydrogen bonding between the flat ring-shaped peptides (Figure 8).^{91–102}

These nanotubes were found to be very robust and turned out to be stable to a wide range of pH and solvents, as well as to physical stress.⁹⁴ From variable temperature studies in chloroform, Ghadiri and co-workers concluded that the dimeric form was favored over the monomer by 23 kJ mol⁻¹, and they postulated that this gain in stabilization energy would be additive as the number of assembled rings increased.⁹⁵ The association constant is dependent on the peptide residue used and is around 2500 M⁻¹. By selective backbone *N*-methylation the self-assembly of the peptides is limited to the formation of dimers.^{96,97} Subsequently linking of two of the *N*-methylated peptides by a short spacer results again in the formation of linear reversible polymers, this time with the direction of chain growth perpendicular to the direction of hydrogen bonding. A clever combination of this approach with the photoisomerization

of an azobenzene unit, resulted in a system that can be switched between intramolecular dimerization and linear polymer formation by UV light.^{98,99} The cyclic peptides were shown to self-assemble in membranes to form trans-membrane ion channels,¹⁰⁰ whose orientation in the membrane has been studied in detail with different IR techniques.¹⁰¹ The nanotubes have been used in size-selective ion-sensing on self-assembled monolayers.¹⁰² Tubular assemblies based on hydrogen bonding between cyclic β -peptides, have been reported by Seebach,¹⁰³ and by Ghadiri who showed that these related structures also self-assemble to form membrane-spanning ion channels.¹⁰⁴ Stable peptide nanotubes have been obtained by using the hydrogen-bond formation between urea groups in cysteine based macrocycles.¹⁰⁵

The groups of Reinhoudt¹⁰⁶ and of Whitesides¹⁰⁷ have reported independently on the formation of supramolecular "nanorods" based on the well-known cyanuric acid–melamine motif. These hydrogen-bonded polymeric rods are composed of parallel cyanuric acid–melamine rosettes (Figure 9).

Both groups employed the same rationale: the self-assembly of dimelamine derivative with a dicyanurate derivative in which the spatial distance between the two cyanurate units is different from the distance between the two melamine units. It was anticipated that this mismatch prevented the formation of a closed disklike assembly and induced the formation

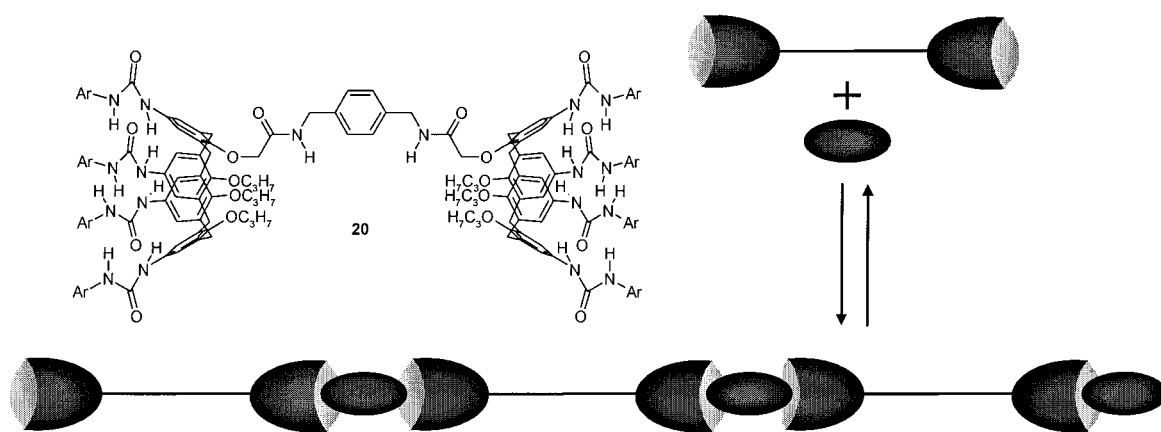


Figure 10. Bifunctional calixarene derivative **20** and a cartoon-like representation of its polymerization induced by small molecules.

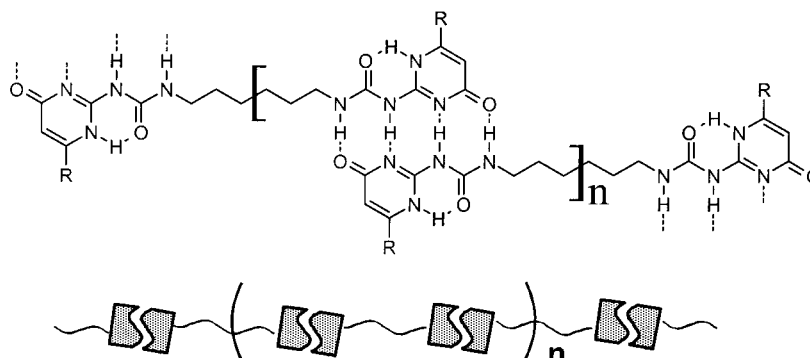


Figure 11. Polymeric assembly of a bifunctional ureidopyrimidinone derivative.

of polymeric entities. A 1:1 mixture of dimelamine (**18**) and dicyanurate (**19**) resulted in a viscous solution, indicating that high-molecular-weight aggregates were formed. The nature of the aggregates was further investigated by NMR spectroscopy, gel permeation chromatography (GPC), and transmission electron microscopy (TEM).

The group of Rebek Jr. has developed an ingenious way to form supramolecular polymers by utilizing the hydrogen bonding between urea functionalized calixarenes (Figure 10).^{108–112} These calixarenes had been shown to form very stable dimeric capsules which bind a solvent molecule inside their cavity. Association of bifunctional molecules consisting of two covalently connected calixarene moieties (**20**) results in the formation of “polycaps”. The association between the monomers is based upon hydrogen bonding in cooperation with complexation of a small guest; the polymerization of the assembly is driven by encapsulation of small guests such as benzene. Solutions of these molecules in *o*-dichlorobenzene show polymer-like rheological behavior, with a strong concentration-dependent viscosity.¹¹¹ The physical integrity of the noncovalent assemblies under shear was demonstrated by the observation of strong normal forces in rheometry experiments. The “polycaps” can be drawn into fibers with a tensile strength in the order of 10^8 Pa.¹⁰⁹ Networks from tetrafunctional molecules in solution display a stronger elastic component in their rheological behavior, and they have complicated time dependent properties such as shear thickening. When the “polycaps” are fitted with

long alkyl chains, chloroform solutions develop liquid crystallinity.¹¹²

Although these supramolecular polymers possess intriguing new properties, synthetic barriers hamper extensive study of the mechanical properties of these materials. The supramolecular polymers discussed above are the products of multistep synthesis, and it is a daunting task to prepare sufficient amounts of material for evaluations such as melt–rheological experiments and tensile testing. The development of the ureidopyrimidinone functionality, a synthetic very accessible quadruple hydrogen-bonding unit with a very high association constant, has helped enormously to open the way to complete exploration of all aspects of supramolecular polymers.

E. Ureidopyrimidinone-Based Polymers

The ureidopyrimidinone unit can be made in a one-step procedure from commercially available compounds,^{29,31} and it dimerizes with an association constant of 6×10^7 M⁻¹ in CDCl₃. Difunctional compounds (**21**), possessing two of these ureidopyrimidinone units, form very stable and long polymer chains in solution as well as in the bulk (Figure 11).^{113,114}

Dissolving a small amount of this low-molecular-weight compound (**21**) in chloroform results in a solution with a high viscosity. It can be calculated that polymers with chain lengths of the order of 10^6 Da can be formed when highly purified monomers are used. The presence of monofunctional impurities

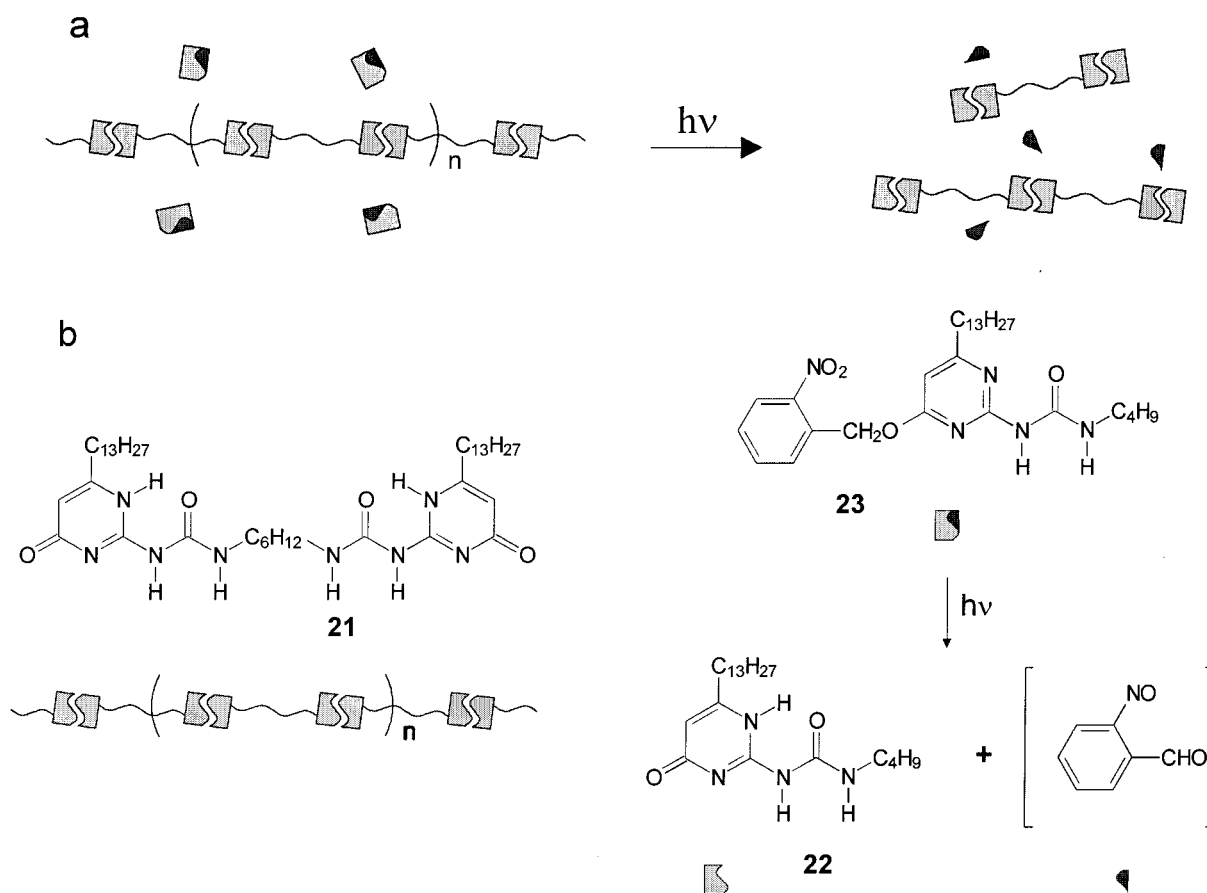


Figure 12. Light-induced depolymerization of UPy-based supramolecular polymers. Concept (a); and compounds used (b).

is expected to lead to a dramatic reduction in DP, because they will act as “chain stoppers”. In fact, deliberate addition of small amounts of monofunctional compounds (**22**) results in a sharp drop in viscosity, proving the reversibility and unidirectionality of association. The reversibility of the linkages between the building blocks is instrumental in the development of materials that change their properties in response to environmental changes, so-called ‘smart materials’. Application of a light-sensitive monofunctional compound (**23**) yielded a material from which the degree of polymerization in solution could be tuned by UV irradiation (Figure 12).¹¹⁵

Although the supramolecular polymers based on bifunctional ureidopyrimidinone derivatives in many ways behave like conventional polymers, the strong temperature dependence of their mechanical properties really sets them apart from macromolecular polymers. At room temperature, the supramolecular polymers show polymer-like viscoelastic behavior in bulk and solution, whereas at elevated temperatures liquid-like properties are observed. These changes are due to a 3-fold effect of temperature on the reversible polymer chain. Because of the temperature dependence of the K_a value of UPy association, the average DP of the chains is drastically reduced at elevated temperatures. Simultaneously, faster dynamics of the scission–recombination process leads to faster stress relaxation in an entangled system. These two effects occur in addition to the temperature-dependent stress relaxation processes that are also operative in melts

or solutions of conventional polymers. Similar to the behavior in the melt, solution viscosities of UPy-based supramolecular polymers are also strongly temperature-dependent. Recently a very surprising inversion of the normal temperature-dependence of the solution viscosity was observed in solutions of preorganized difunctional compounds (**24**), which form a mixture of linear polymer chains and cyclic dimers (Figure 13).¹¹⁶ The thermodynamic parameters of this equilibrium are such that polymerization is favored at higher temperatures. As a result, the viscosity of a 145 mM chloroform solution of the compound was observed to increase by a factor of 3.9 when the temperature was increased from 255 to 323 K. Entropy-driven polymerizations are rare, and the unexpected effect in this system is the first time it was observed in a reversible synthetic system.

The quadruple hydrogen-bonded unit has been further employed in the chain extension of telechelic polysiloxanes,¹¹⁷ poly(ethylene/butylenes), polyethers, polyesters, and polycarbonates.¹¹⁸ In these compounds, the material properties were shown to improve dramatically upon functionalization, and materials were obtained that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds. This strategy can be seen as closing the gap between polymers and oligomers by taking the best of both worlds. Especially in the field of conjugated polymers for plastic electronic devices, expectations for future applications of this strategy are high.¹¹⁹

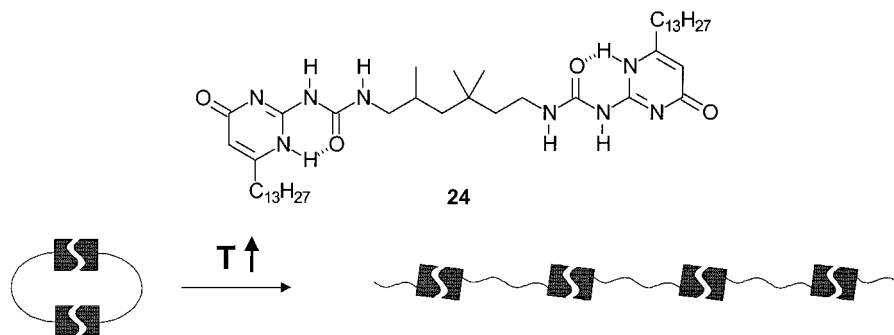


Figure 13. Entropy-driven ring-opening polymerization of the cyclic dimer of **24**.

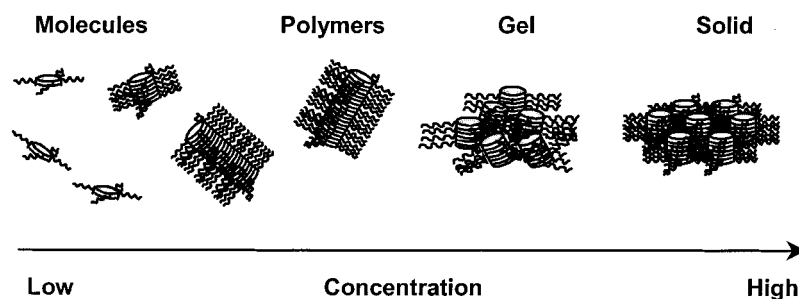


Figure 14. Self-assembly of discotic molecules with the different aggregates given as a function of concentration.

Very recently, Coates et al. used a vinyl-substituted Urypic unit to be part of an olefin polymerization using the Brookhart catalyst. With small amounts of Urypic units incorporated, the polyolefins showed thermoplastic elastomeric properties.¹²⁰

The reversibility of supramolecular polymers adds new aspects to many of the principles that are known from condensation polymerizations. A mixture of different supramolecular monomers, for example, will yield copolymers, but it is extremely simple to adjust the copolymer composition instantaneously by adding an additional monomer. Moreover, the use of monomers with a functionality of three or more, will give rise to a network formation. However, in contrast to condensation networks, the “self-healing” supramolecular network can reassemble to form the thermodynamically most favorable state, thus forming denser networks.¹²¹

Although the “virtual” molecular weight and lifetime of supramolecular polymers and networks based on strong hydrogen-bonding functionalities is extremely high, low creep resistance is an intrinsic property of these materials that may limit future applications. Strong interchain interactions, especially in crystalline domains, may be employed to tackle this problem and may lead to thermoplastic elastomers with enhanced processability. With the facile synthetic accessibility of these self-complementary Urypic units at hand it is expected that many novel materials properties can be obtained, and multiple hydrogen bonding between repeating units offers an ideal motive for supramolecular polymers, both in solution and in the solid state.

V. Supramolecular Polymers Based on Discotic Molecules

Discotic molecules are ditopic structures with a disc-shaped core and a periphery of a number of

flexible side-chains. The core generally consists of a planar aromatic system, whereas the side-chains are usually flexible alkyl chains.¹²² This anisotropy generates thermotropic liquid crystalline mesophases, as was first discovered in 1977. The structural properties make discotic molecules highly suitable for the formation of supramolecular polymers in solution. The strong π - π (or arene-arene) interactions of their cores make discotics prone to aggregate in either polar or apolar solvents, forming rodlike or wormlike polymers. Because of the polarizability and good intermolecular contact of the planar aromatic system attractive intermolecular stacking interactions occur. In polar or in very apolar solvents the π - π stacking may be strengthened significantly by solvophobic interactions. In this section we will use the general term arene-arene interactions, but it should be noted that solvophobic effects are generally stronger than π - π stacking.

Actually, discotic liquid crystals are the only type of liquid crystals able to form linear architectures, i.e., supramolecular polymers, in dilute solution by means of these stacking interactions. Other types of liquid crystals have ordering interactions of the same order of magnitude in at least two dimensions. This gives rise to gels at appreciable concentration, i.e., uncontrolled growth of the aggregates, whereas at lower concentrations the intermolecular interactions are generally too weak to generate polymeric architectures.

In discotics, the interdisk stacking interaction is several orders of magnitude stronger than the intercolumnar interactions, because of the phase separation induced by the side-chains whose van der Waals interactions are much weaker. Generally, long polymers are obtained via discotics that have strong and specific intermolecular interactions, either via a large aromatic core or via additional specific intermolecular

interactions such as hydrogen bonding. Moreover, the combination of two or more interactions accounts for the formation of highly ordered columns. Only at higher concentrations, the intercolumnar interactions become prominent, and superstructure formation or gelation occurs followed by the liquid crystalline phase in the bulk. An illustrative picture displaying the self-assembly of discotic molecules into supramolecular polymers is given in Figure 14.

In this section we will discuss those discotic molecules that have been shown to form supramolecular polymers. For information concerning discotic liquid crystals in general, their synthesis, behavior, and applications the reader is referred to review the literature.¹²² The mechanical properties of the supramolecular polymers from discotic liquid crystalline molecules are not particularly interesting and have not been studied in detail, therefore, these properties will not be covered here. It should be noted, however, that because of the strong intermolecular interactions, the thermotropic mesophases of discotics generally show much better mechanical properties than those of calamitics, illustrating the beneficial properties of strong unidirectional interactions. Because the specific interactions between the disks in the rigid-rod supramolecular polymers often gives rise to well-defined architectures, we will discuss the architectures of these supramolecular polymers in more detail.

This section is divided into three parts. The first part, section A, deals with rodlike polymers formed by the arene–arene interactions. In the second part (B) discotics will be discussed for which unidirectional hydrogen bonding is the driving force for supramolecular polymerization. Finally, section C will deal with supramolecular polymers formed by a combination of arene–arene interactions and hydrogen bonding.

A. Arene–Arene Interactions

1. Triphenylenes

Alkoxy substituted triphenylenes (**25a–e**) were among the first discotic molecules shown to be liquid crystalline.^{123,124} A large variety of different triphenylenes has been synthesized and their thermotropic mesomorphism has been studied in great detail.¹²² The aromatic core of triphenylenes is relatively small; nevertheless, polymerization of triphenylenes (**25a–c**) does occur in deuterated hexadecane as shown with small angle neutron scattering (SANS).¹²⁵ At low concentrations the DP is small, but at higher concentrations (10^{-3} M) rodlike polymers are observed. The intercore distance was determined to be ~ 6 Å, a value significantly larger than the stacking distance of ~ 3.5 Å in the liquid crystalline state. This result indicates that the molecules are loosely stacked, most probably due to the absence of specific intermolecular interactions. Furthermore, the triphenylenes are highly mobile and undergo both lateral and rotational translation, similar to that in the liquid crystalline state.¹²⁶ The supramolecular polymerization of triphenylenes was also visualized using optical techniques. Increase of the concentration of a solution of

triphenylene **25d** resulted in a broadening of the UV–Vis spectrum and an increase of the absorbance.¹²⁷

Ringsdorf and co-workers have shown that triphenylenes can form alternating donor–acceptor supramolecular polymers in solution by doping them with equimolar amounts of electron acceptors.^{128,129} Supramolecular polymers formed in this manner allow for electron transfer perpendicular to the molecular planes upon excitation of the chromophores, i.e., unidirectional charge-transport through the column.¹³⁰ The formation of these donor–acceptor pairs is favored in apolar solvents. In more polar solvents the triphenylenes alone do not polymerize and consequently donor–acceptor polymers with low DP are formed.

The “loose” way of stacking of the triphenylenes was shown by the absence of a Cotton effect in circular dichroism (CD) experiments for chiral triphenylene **25e** in heptane.¹³¹ Even though this chiral molecule does form a supramolecular polymer, the side-chain chirality is not expressed in the column: a phenomenon typical for molecules arranged in an unordered assembly. Mixing of achiral alkoxytriphenylene **25d** with a bulky chiral electron acceptor derived from (–)-menthol 3,5-dinitrobenzoate (**26**) did introduce supramolecular chirality in the columns.¹²⁷ The sterically demanding “bulky” menthol group intercalates in the alkyl side-chains of the triphenylene and induces a noncooperative helical twist into the columns (Figure 15), resulting in an induced CD effect in the chromophore of the triphenylene.

Triphenylenes provided with nonionic di(ethylene oxide) side-chains (**25f**)^{132–134} or with ionic alkyl chains (**25g**)¹³⁵ form supramolecular polymers in water.¹³⁶ The arene–arene interactions of the aromatic cores allow for the formation of columnar “micelles”. At low concentrations the columns are relatively short, and the solutions are isotropic. At higher concentrations the longer columns interact and lyotropic mesophases are formed.¹³³ Computer simulations showed that in the isotropic solution the polymerization of the discotics is driven by solute–solute attraction and follows the theory of isodesmic linear aggregation; the association constants for dimerization, trimerization, and etc., are equal and the DP of the column thus can easily be tuned by concentration and temperature.^{137,138} At higher concentrations the sizes of the columns are influenced by their neighbors, the columns align, and the DP rises rapidly.

Fluorescence studies have shown that the radiative lifetime of **25f** increases upon increasing DP, suggesting that the mobile excitons move through the supramolecular polymers and relax at their ends.¹³⁹ Insertion of electron acceptors between the triphenylenes accounts for the formation of longer polymers and increases the order within the column. An X-ray diffraction ring with a diffraction spacing of 3.5 Å indicates a short intermolecular distance, a feature not present for undoped samples.¹⁴⁰ A chiral electron acceptor resulted in the formation of a cholesteric mesophase.

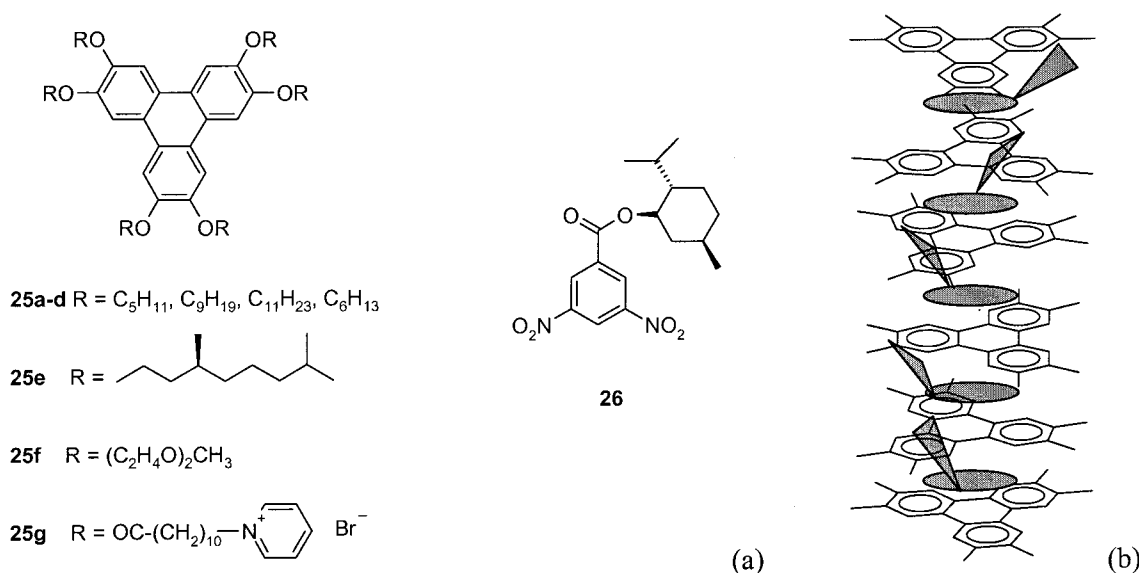


Figure 15. (a) Apolar (**25a–e**) and polar (**25f–g**) triphenylenes and electron acceptor (–)-menthol 3,5-dinitrobenzoate (**26**). (b) Helical columns based on the donor–acceptor system as studied by Schuster.

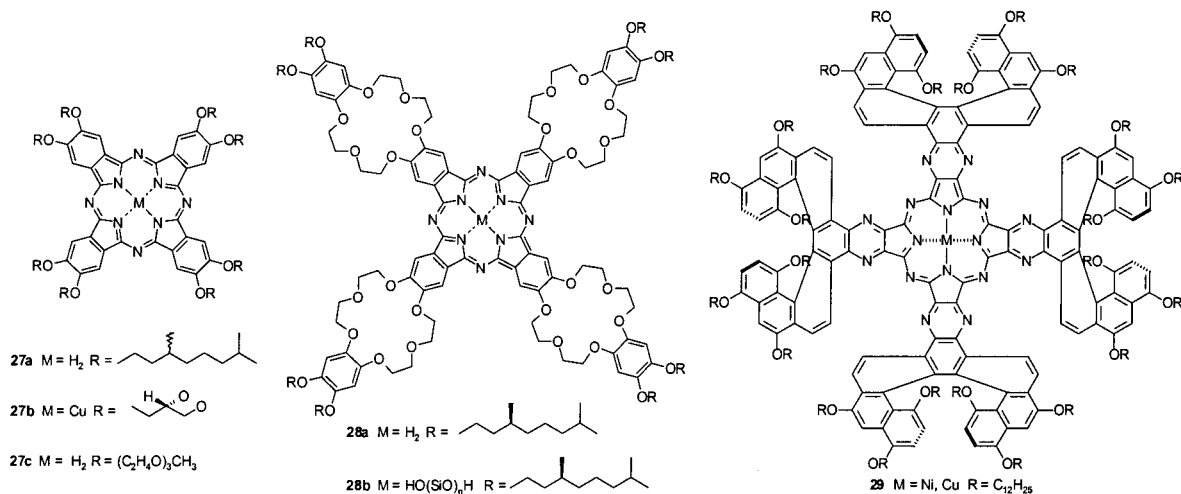


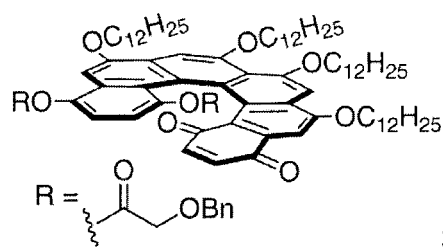
Figure 16. Extended-core phthalocyanine discotics **27–29**.

2. Phthalocyanines and Porphyrins

With respect to triphenylenes, phthalocyanines have a significantly larger core, in principle generating stronger intermolecular arene–arene interactions.¹⁴¹ Moreover, their optical and electrical properties can be easily tuned by incorporation of a metal in the core. The aggregation of nonliquid crystalline phthalocyanines in both water^{142,143} and in organic solvents^{144,145} has been studied intensively in the past; and more recently the formation of Langmuir–Blodgett^{146,147} films and the aggregation of liquid crystalline compounds also have been investigated.^{148–150} In contrast to the isodesmic aggregation of triphenylenes, phthalocyanines show a nonisodesmic behavior as they preferably dimerize and do not form oligomers until much higher concentrations.^{151–156} Experiments on Langmuir–Blodgett films of phthalocyanine **27a** have indicated that large columnar aggregates are present (Figure 16), but that they consist of repeating oligomers built up from two to six molecules.¹⁵¹ Apparently, dimerization significantly lowers the intermolecular affinity of phthalocyanines,

and only in phase-separated systems such as gels, or in the solid, are long supramolecular polymers formed.¹⁵⁷

Interestingly, it has been possible to obtain helical phthalocyanine polymers. By locking the position of phthalocyanines, rotation is prevented. Amphiphilic, chiral metallophthalocyanine **27b** dissolves molecularly in DMSO, but addition of water results in the formation of a helical dimer.¹⁵⁸ In the twisted helical stacks, rotation is no longer possible because of intermolecular hydrogen bonding. At higher concentrations polymeric fibrous assemblies are formed. For apolar analogues in apolar solvents similar chiral dimers and higher aggregates have been obtained.¹⁵⁹ By providing the phthalocyanine with a periphery of crown ethers^{160,161} and chiral alkoxy side-chains (**28a**), self-assembly in helical aggregates occurs, as was deduced from the emergence of a Cotton effect and large helices observed with electron microscopy at higher concentrations.¹⁶² The side-chains induce a twist in the aggregate because of steric interactions since the aggregates formed by their achiral coun-



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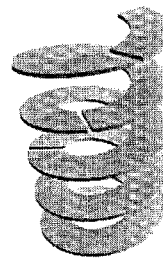


Figure 17. Liquid crystalline disc-shaped helicene **30** and its mode of association into helical columns. (Reprinted with permission from ref 189. Copyright 2000 John Wiley & Sons, Inc.)

terparts are not helical.¹⁶³ The helicity of this aggregate could be “turned off” by the addition of potassium salt, overruling the twist imposed by the chiral side-chains, with the ion–dipole coordination of potassium ions to two crown ether rings of two different phthalocyanines. The unwinding of the helical aggregate results in a nonassociating achiral dimer. In contrast, the supramolecular chirality of covalent polymer **28b** remains present upon the addition of potassium ions, illustrating the ease of tuning the properties of supramolecular polymers via external stimuli.¹⁶⁴

Providing phthalocyanines with chiral bulky helicenes at the periphery (**29**) also results in helical aggregates.¹⁶⁵ Aggregation in chloroform occurs upon addition of ethanol as was observed with UV–Vis spectroscopy, while CD spectroscopy revealed the helical nature of the columnar aggregates. Calculations have indicated that two phthalocyanines need to be rotated to allow a favorable intermolecular distance of 3.4 Å, because of the bulky helicenes. As such, phthalocyanines provided with racemic helicenes cannot stack in such a defined manner, because of the steric hindrance of the racemic side groups. Aggregation of a smaller analogue of **29**, a triphenylene-based porphyrazine, has been shown to occur as well.¹⁶⁶

Polymerization of phthalocyanines in water occurs for derivatives substituted with oligo(ethylene oxide) side-chains (**27c**).^{167,168} In the lyotropic mesophases in water supramolecular polymers are present, and a comparative aggregation study between tetraphenylporphyrins and phthalocyanines proved the polymerization of the phthalocyanines to be stronger.¹⁶⁸ The strong arene–arene interactions and the flatness of the aromatic core in the phthalocyanines causes them to aggregate more strongly, also mediated by the additional hydrophobic effect.

Porphyrins are close analogues to the phthalocyanines, and ionic porphyrins can be considered to fall into the class of the chromonics (vide infra), however, nonionic porphyrins also have been shown to aggregate.¹⁶⁸ Also, porphyrins are mainly forming dimers in solution,^{169,170} although aggregation into larger aggregates such as fibers has been shown.¹⁷¹ Within the aggregates the molecules are rotating freely, but use of additional interactions such as intermolecular hydrogen bonding hinders the rotation and generates chiral aggregates.¹⁷¹

3. Helicenes

Nonracemic helicene **30** has been shown to form supramolecular polymers, and the helical shape of

their rigid cores renders these columns helical (Figure 17).¹⁷² The high DP at high concentrations in dodecane results in an increase of the viscosity and an increase of the Cotton effect as observed with CD spectroscopy. The helical supramolecular polymer gives rise to a stronger expression of chirality, because the intrinsic shape of the helicenes generates a tight “intertwined” fit. More detailed measurements have been performed on columns formed by a non-liquid crystalline helicene.^{173–175} These supramolecular polymers have been proven to be extremely promising systems for second-order nonlinear optics. They form highly organized Langmuir–Blodgett films in which the chiral polymeric organization makes the second-order NLO susceptibility approximately 30 times larger for the nonracemic material than for the racemic material with the same chemical structure.¹⁷⁶

4. *m*-Phenylene Ethynylene Oligomers

Whereas helicene **30** studied by Katz¹⁷² is helical under all conditions, the *m*-phenylene ethynylene oligomers studied by Moore are flexible and can reversibly fold into helices. Depending on the substitution pattern, the oligomers fold either into lamellae (**31a**)¹⁷⁷ or into column-forming helices (**31b**)¹⁷⁸ in the liquid crystalline state (Figure 18). In solution the oligomers can be directed to fold from a random coil into a helix.^{179,180} Increasing the polarity by addition of water (a nonsolvent for the backbone) results in the polymerization of the helices in helical columns.¹⁸¹ The polymerization of the oligomers is a cooperative process: a chiral oligomer **31c** creates a homochiral platform for an achiral oligomer **31a** to stack and thus amplifies its chirality to the achiral oligomer. Also, apolar *m*-phenylene ethynylene oligomers **31d** fold into helices.¹⁸² Because of the strongly favored arene–arene interactions in apolar solvents, the helical folding coincides with stabilizing stacking of the oligomers into helical columnar polymers, giving a strong and time-dependent enhancement of the Cotton effect.

Cyclic *m*-phenylene ethynylene oligomers **32** adopt a completely flat conformation (Figure 19) and form highly stable thermotropic mesophases due to strong π – π stacking of the cores.¹⁸³ These arene–arene interactions also induce polymerization in solution.¹⁸⁴ The DP depends heavily on the nature of the substituents on the macrocycle.¹⁸⁵ Planarity is a strict requirement for polymerization as the DP is strongly suppressed for nonplanar macrocycle **33**.¹⁸⁶ Butadiyne bridged macrocycles with benzenes (**34**) or with pyridines (**35**), the larger analogues of the *m*-phen-

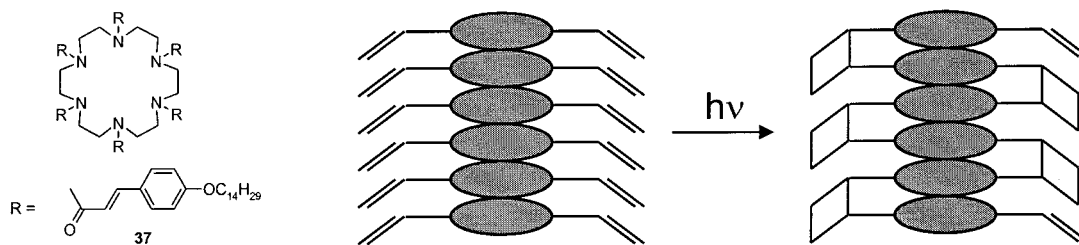


Figure 21. Hexa-cinnamoyl azacrown with polymerizable side-chains **37** as studied by Ringsdorf, and the photopolymerization into covalent columns in solution.

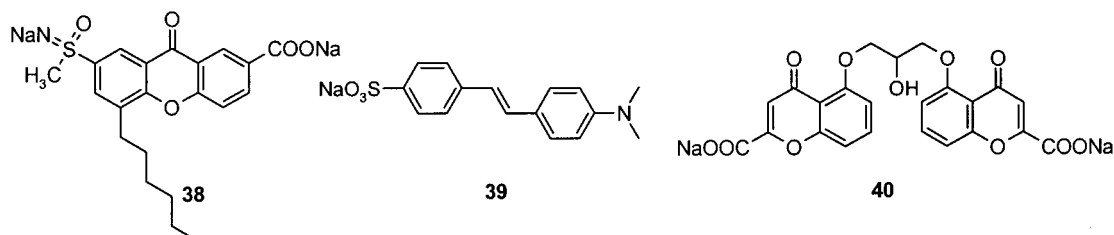


Figure 22. Examples of drug and dye molecules forming chromonic mesophases in water.

As early as 1986, the aggregation in solution of an alkyl modified 2,6,2',6'-tetraphenyl-[4,4']-bipyranilidene was shown, and the self-assembly was related to its thermotropic mesomorphism.¹⁹³ The addition of the more polar solvent methanol to methylene chloride induces aggregation into J aggregates. As the nonliquid crystalline compound without the side-chains does not aggregate, it might be concluded that the self-assembly is, in this case, not dominated by the aggregation of the aromatic core. Self-assembly via aggregation of the side-chains occurs, which is fundamentally different from the previously discussed polymers, and generally leads to 3-dimensional growth.

A variety of smaller discotic molecules have been shown to form lyotropic mesophases in either alkane solvents or water. These discotics range from alkyl-oxidybenzopyrenes¹⁹⁴ and hexaesters of hexahydroxybenzene and -cyclohexane¹⁹⁵ to metallo-discogens.¹⁹⁶

6. Chromonics

Discotic molecules provided with oligo(ethylene oxide) side-chains form supramolecular polymers in water. If the discotics are provided with ionic groups the compounds are known as chromonics (for examples see **38–40**, Figure 22).^{197,198} Even though chromonics are crystalline and do not form supramolecular polymers in the solid state, we mention them briefly here because of their practical importance and widespread occurrence. A large body of work, dating back to the early part of the 20th century, has been performed on these compounds, and the reader is referred to review articles for detailed information.^{197,198} The most common chromonics are drugs and dyes, which explains the early recognition of their aggregation. Their self-assembly in water makes them a highly important type of lyotropic liquid crystal, as it influences their performance. The molecules first self-assemble, isodesmic, into supramolecular rodlike polymers, followed by the formation of lyotropic mesophases. The rodlike polymers

induce a strong increase in the viscosity of the solution, and the dynamic properties of these aggregates leads to rheological behavior typical for entanglement networks.¹⁹⁹ The observations have indicated that chromonics are suited as simple model systems for a broader and deeper insight into the principles of flow.

B. Hydrogen Bonding

Section V–A has dealt with the formation of supramolecular polymers by nonspecific arene–arene stacking, which generally results in irregular or “loose” stacking. The use of additional steric interactions in these structures allowed for a control over supramolecular order or helicity. In this section we will discuss columnar supramolecular polymers formed by the more specific intermolecular hydrogen bonds.

The main body of work on columnar hydrogen-bonded architectures has been performed on 1,3,5-benzene triamides (**41**), which are C_3 -symmetric molecules consisting of a single benzene ring and 3 side-chains connected via amide bonds.^{200,201} The molecules arrange themselves in columns via 3-fold intermolecular hydrogen bonding as proven by X-ray diffraction²⁰² and infrared spectroscopy. The weak arene–arene interactions of the single central benzene group are subordinate to the strong 3-fold hydrogen bonding. For packing reasons, the intermolecular hydrogen bonds rotate out of the plane, thus inducing helicity in the columns. Achiral compounds **41a–d** form an equimolar mixture of left- and right-handed helical columns, but the homochiral side-chains of chiral discotic compound **41e** introduce an energy difference between left and right-handed columns and bias the helicity.²⁰³ Figure 23 shows the formation of the helical columnar polymers by the polymerization of **41d** in a cartoon-like presentation.²⁰²

The helical rigid-rod polymers have a high DP even in very dilute solution (10^{-6} M in hexane), due to their large association constant ($5 \cdot 10^8$ L/mol). When

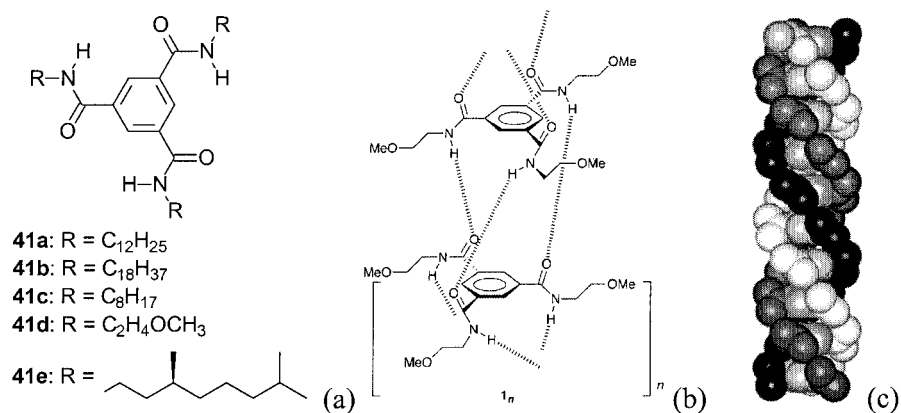


Figure 23. (a) 1,3,5-Benzene trisamides that form columns in apolar solvents via 3-fold intermolecular hydrogen bonding; (b) solid state arrangement of the helical columns; (c) graphical representation of the helical hydrogen-bonded columns. (Reprinted with permission from ref 202. Copyright 1999 Royal Society of Chemistry.)

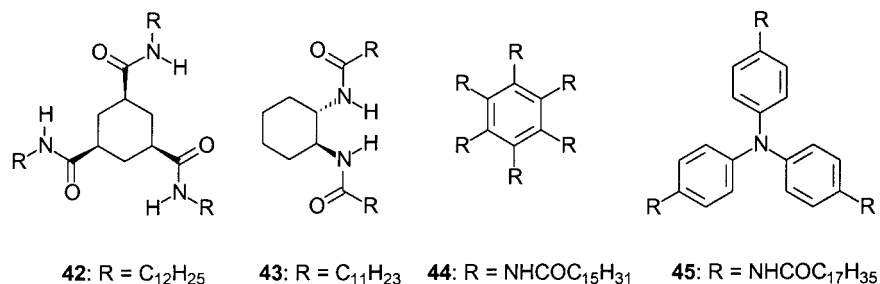


Figure 24. Small discotics that form columnar polymers via intermolecular hydrogen bonding.

chiral (**41e**) and achiral (**41c**) molecules are blended mixed columns are formed, and, surprisingly, only one chiral disk (on average) on every 200 achiral disks is enough to bias the helicity of a complete columnar polymer for one helicity. These results are analogous to those obtained in chiral polymers with covalent bonds in the main chain²⁰⁴ and are explained by a strong intracolumnar cooperative effect via directional hydrogen bonding in polymers with a very high DP. At higher concentrations, the long columns gelate the solvent via lateral intercolumnar interactions,^{200,201} reminiscent of the behavior of rigid-rod covalent polymers such as polyaramides and poly(γ -benzyl-L-glutamate).²⁰⁵

Cis-1,3,5-cyclohexanetricarboxamides (**42**) are another example of discotic molecules assembling in columns via intermolecular hydrogen bonding (Figure 24).²⁰⁶ Because of the cis arrangement of the amides, all three can participate in the uni-directional hydrogen bonding. Depending on the type of solvent, the compound either gels the solvent or forms a transparent viscoelastic fluid. No mention is made of the presence of helicity in the columnar aggregates or at a microscopic level, in contrast to the trans-1,2-diaminocyclohexane derived gelators (**43**), which form chiral supercoiled structures observable with electron microscopy.²⁰⁷

Aggregation via hydrogen bonding and formation of columns and lyotropic liquid crystals and gels has also been described for benzenehexamine derivatives **44**²⁰⁸ that assemble via 6-fold intermolecular hydrogen bonding, and for tris(stearoylamino)triphenylamine **45**²⁰⁹ that assembles via 3-fold intermolecular hydrogen bonding.

C. Arene–Arene Interactions and Hydrogen Bonding

Although hydrogen bonds can be employed for the creation of highly ordered columns (section V–B), their use is highly limited to apolar solvents. In contrast, arene–arene interactions allow for supramolecular polymer formation in a large variety of solvents, but without positional control (section V–A). Thus, the combination of arene–arene interactions and hydrogen-bonding should allow for formation of highly ordered supramolecular polymers with high DP in solvents as desired. In this section we discuss such supramolecular polymers. Hydrogen bonding has been utilized both for the formation of the discotic entity itself and as a tool to control the order within the columns. Furthermore, the occurrence of hydrogen bonds allows for a controlled hierarchical growth of the well-defined columns, and subtle tuning of the interactions can be achieved by selection of solvent type.

1. Guanine and Pterine Derivatives

The most impressive work on self-assembling chiral discotics has been performed on guanine- and pterine-related molecules by Gottarelli, Spada, and co-workers.²¹⁰ These molecules organize in lamellae in the solid state,^{211,212} but form disc-shaped tetramers in solution via intermolecular hydrogen bonding. The subsequent stacking of the disks into helical columns has been most elaborately studied. The system is of interest because of its strong similarities to DNA and other biopolymers.^{213,214}

Oligomeric deoxyguanosines **46** all assemble into columns in water.²¹⁵ Using SANS, the average length

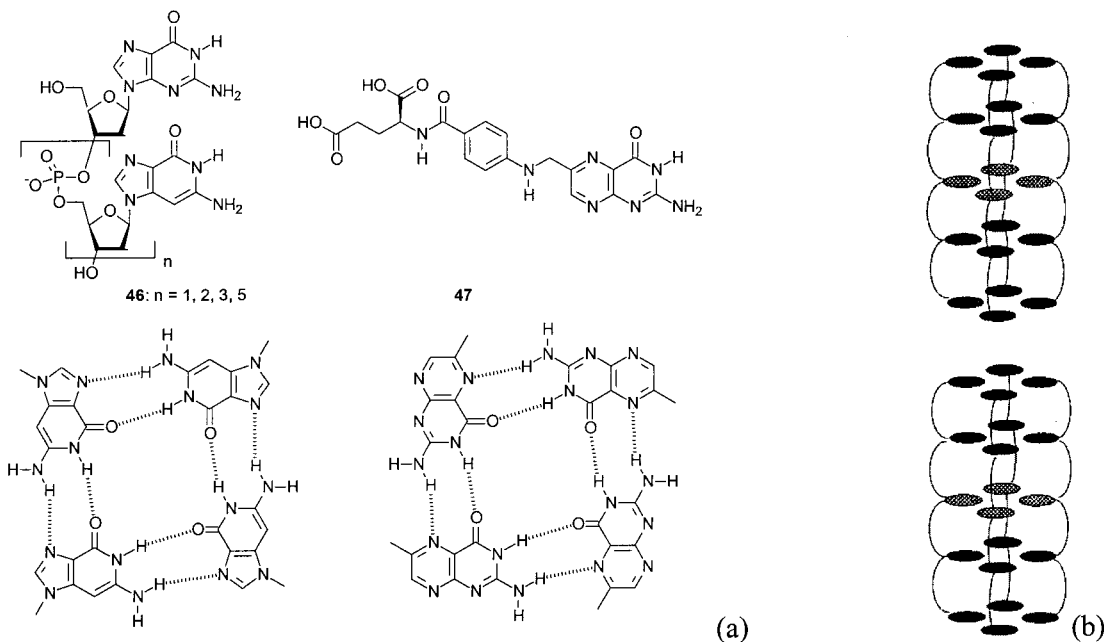


Figure 25. (a) Deoxyguanosine oligomers **46** and folic acid **47** and their mode of self-assembly in tetramers; (b) mode of aggregation of eight d(GpGpApGpG) molecules. First, self-assembly in “barrels” occurs, followed by stacking of these “barrels” in columns. (Reprinted with permission from ref 222. Copyright 1995 Royal Society of Chemistry.)

of the columns (DP) of freshly prepared samples was determined to be around 6 nm at a concentration of 1% in D₂O.²¹⁰ Increase of the temperature resulted in loss of the cylindrical aggregates. When the sodium salt is used, subsequent cooling does not result in the re-formation of the cylindrical polymers. In contrast, use of the potassium salt does allow for reversible self-assembly. The addition of extra potassium salt even increases the DP; it binds to the inner carbonyls of the G-tetramer and stabilizes the tetramer.²¹⁶

The formation of lyotropic liquid crystalline mesophases by a deoxyguanosine derivative in water was reported in 1988,²¹⁷ after which this behavior was found for other monomers and oligomers of deoxyguanosine phosphate.²¹⁸ The microscopic textures observed show the presence of cholesteric and hexagonal phases at lower and higher concentrations, respectively. The polymeric columns are formed in a hierarchical manner: first a well-defined “barrel” is formed by the assembly of four oligodeoxyguanosine oligomers, and then these “barrels” stack on top of one another to give the columns (Figure 25 b).^{210,215} This stepwise self-assembly process was elucidated using CD experiments, which revealed two melting transitions. Furthermore, it was shown that formation of the liquid crystalline phase depends on the amount of electrostatic repulsive interactions from the phosphate groups and the hydrophilic/hydrophobic balance.

Not only guanosine, but also pterine derivatives, give rise to supramolecular polymers in water.²¹⁹ Similar to the guanosines, folic acid **47** assembles in disc-shaped tetramers in water. Addition of sodium or potassium salts aids the tetramerization and induces the aggregation into columns.²²⁰ At the relatively high concentration of 4%, w/w, these columns have an average DP of 9 disks. Melting experiments performed in water and upon the addition of salt showed very interesting results. The

intensity of the Cotton effect was followed as a function of temperature, indicating the amount of chirality present in the columns. In water a single melting transition was detected, whereas in the presence of salt two melting transitions were visible, indicating hierarchical assembly.²²¹

Gottarelli, Davis, and co-workers have prepared apolar guanosine derivatives **48a** and **b** for study in organic solvents. In dilute solution in the presence of potassium ions, disc-shaped structures are formed.²²² In chloroform compound **48b** is molecularly dissolved, but upon contact of the organic layer with an aqueous layer containing potassium salts, **48b** extracts the potassium into the organic layer. An octameric potassium complex is formed, consisting of two stacked G-quartets between which a potassium ion is sandwiched via interactions with the carbonyls of the guanines (Figure 26).^{223,224} Upon the addition of more salt the octamers polymerize into a columnar architecture. In this polymer potassium ions and G-quartets alternate in the stacking.²²⁵ The Cotton effect observed for the polymer indicates a helical columnar nature. Apart from the formation of octamers, the formation of decamers has also been observed.²²⁶

Compound **48b** was shown to display enantioselectivity in the extraction of chiral potassium salts from water into the organic phase.²²⁷ The supramolecular polymer possesses a homochiral helical architecture onto which one of the anionic enantiomers preferentially binds. Intriguingly, for some of the anions the octamer and polymer show opposite selectivity, illustrating the difference in supramolecular chirality of the two. Furthermore, the polymer is capable of inducing a Cotton effect in the achiral potassium *N*-(2,4-dinitrophenyl)glycinate. The use of these polymers as artificial ion channels is currently under investigation, as the apolar side-chains would allow incorporation into a membrane.^{224,228} Also,

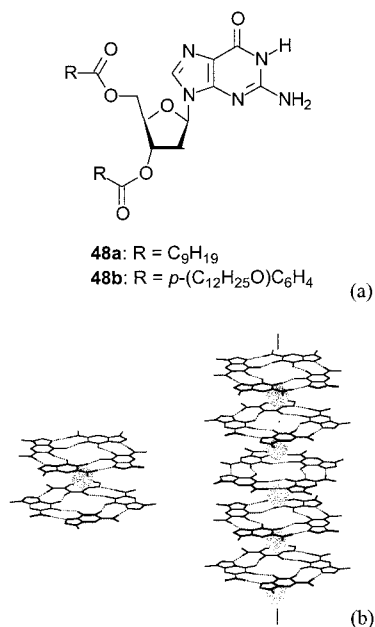


Figure 26. (a) Apolar modified deoxyguanosines, soluble in organic solvents; (b) self-assembly of apolar deoxyguanosines in octamers and polymers upon the addition of potassium ions. (Reprinted with permission from ref 225. Copyright 2001 John Wiley & Sons, Inc.)

these helical columns are ideal supramolecular polymeric architectures for the creation of functional arrays. By providing the guanosines with apolar porphyrins, self-assembly into columns with a periphery of porphyrins was achieved in chloroform by the addition of potassium salt.²²⁹ The formation of such functional polymers using external stimuli offers a unique approach for the creation of bio-inspired self-assembled polymers.

2. Hydrogen-Bonded Pairs

Similar to the guanosine and pterine derivatives, intermolecular hydrogen bonding generates discotics based on molecules **49**. Two molecules **49** dimerize via quadruple intermolecular hydrogen bonding resulting in an extended-core discotic liquid crystal that stacks in apolar solvents and forms columnar supramolecular polymers.²³⁰ Within these columns the discotics are rotating freely. When two hydrogen-bonding units are connected via a short spacer, a bifunctional molecule is generated (**50**), capable of forming hydrogen-bonded, supramolecular polymers

in chloroform similar to the bifunctional ureidopyrimidinones **21** discussed in section IV-E.¹¹³ The disks are in an alternating array of disks and spacers, and they stack in apolar solvents forming a columnar polymer. The columns are helical, in contrast to those formed by monofunctional molecules **49** (Figure 27). The presence of a covalent linkage between consecutive layers of the column prevents rotation of the disks. A comparison might be made here to the function of the sugar–phosphate backbone in DNA.

The intrinsic helicity of the columns formed by bifunctional **50** allows chiral side-chains to control for a preferred handedness (**50b**). The supramolecular polymeric backbone also accounts for a higher DP with respect to monofunctional **49**, as could be observed with SANS and an increased thermostability of the lyotropic mesophase in dodecane. The induction of chirality in the helical columns of **50b** by the chiral side is a cooperative process via the backbone: the helicity of a racemic mixture of helical columns of achiral **50a** is biased when end-capped with monofunctional chiral **49b**.

Helical columns of bifunctional ureidotriazines could also be created in water.²³⁰ In water the aromatic cores of compound **52** stack and create a hydrophobic environment that favors the formation of intermolecular hydrogen bonds. The chiral side-chains can express their chirality within the columnar polymer because of the backbone-generated helicity. In contrast, for monofunctional **51** water interferes with the hydrogen bonding and **51** does not dimerize nor polymerize until it reaches highly elevated concentrations. The bifunctional nature of **52** allows for a high local concentration of stacking units. A comparison might be made here to the individual DNA bases that also do not dimerize and stack in water, unless they are connected to a polymer backbone.

3. Complexation of Tetrazoles with 1,3,5-Tris(4,5-dihydroimidazol-2-yl)benzene

Another example of supramolecular columnar polymers formed by the combined use of hydrogen bonding and arene–arene interactions are the complexes of tetrazoles and 1,3,5-tris(4,5-dihydroimidazol-2-yl)benzene (**53**, Figure 28).²³¹ Four molecules self-assemble to give a supramolecular disc-shaped molecule, which subsequently polymerizes into columns when in nonpolar solvents. Upon formation of a

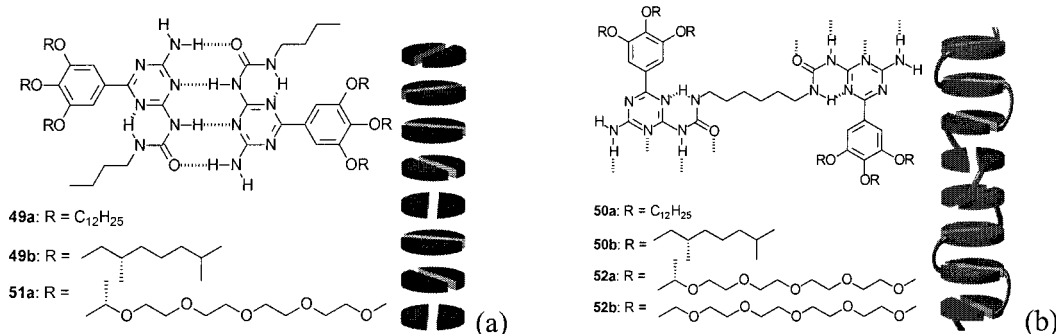


Figure 27. (a) Monofunctional ureidotriazines **49** and **51** and the mode of association of **49** via quadruple hydrogen bonding in a disk and stacking of the disks in columns lacking positional order; (b) bifunctional ureidotriazines **50** and **52** and the helical columns formed by these molecules in which the disks are positionally ordered.

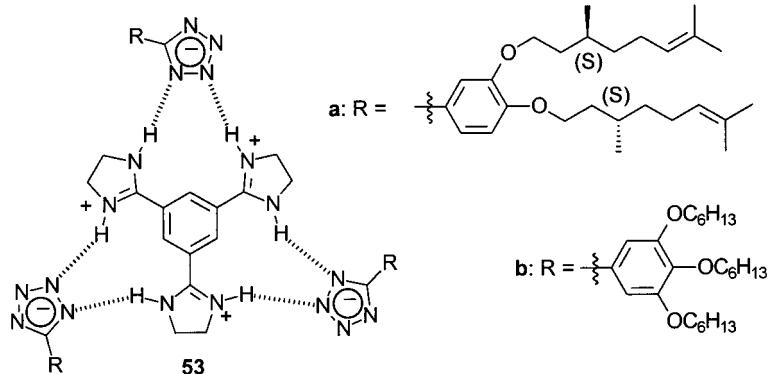


Figure 28. Extended-core discotic **53** built up via intermolecular hydrogen bonding.

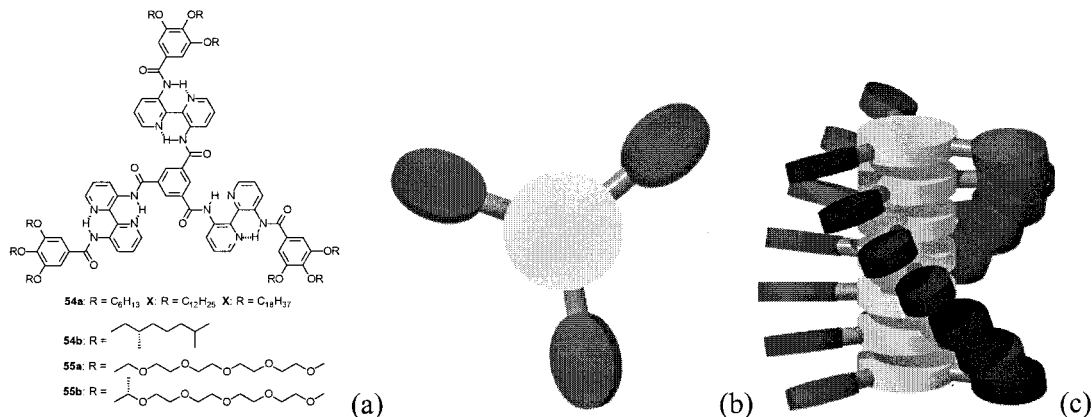


Figure 29. (a) C₃-symmetrical disc-shaped molecules **54** and **55** with achiral and chiral side-chains; (b) a cartoon representation of the propeller-like conformation attained by the C₃-symmetrical molecular; and (c) formation of helical columns by the propellers. (Reprinted with permission from ref 237. Copyright 2000 American Chemical Society.)

columnar aggregate of the chiral disks **53a**, the chirality of the side-chains induces a bias in the helicity of the supramolecular assembly. “Sergeant and soldiers” measurements²⁰⁴ were performed and showed that there is no amplification of chirality from **53a** to **53b**; the induction of helicity in columns of **53** is a noncooperative process.

4. C₃-Symmetrical Discotic Molecules

Molecules that have the best potential for a high degree of polymerization and for the creation of a well-defined architecture in all solvent types need to have a large aromatic core, as well as structuring intermolecular hydrogen-bonding interactions. Disc-shaped molecules **54** and **55** feature these requirements. Discotic molecules **54**²³² form polymeric structures with a rigid-rod character and large DP in very dilute solution (10⁻⁶ M in hexane), due to their large (10⁸ L/mol) association constant.²³³ The aggregation of the disks is a cooperative process; the molecules attain a chiral, propeller-like conformation (Figure 29) and the conformation of subsequent monomers is biased toward a propeller with the same handedness. The optimized stacking interactions result in a helical column. The chirality placed in the side-chains of **54b** accounts for the formation of homochiral columns via the transfer of the side-chain chirality into the supramolecular helical polymer. Using “sergeant and soldiers” experiments²⁰⁴ for mixtures of **54a** and **54b**, the presence of only one disk with chiral side-chains per 80 achiral disks is

enough to obtain helical polymers of one helicity exclusively. This experiment shows that there is a high energetic penalty for helix reversal within the polymer. Lateral interactions between the supramolecular polymers arise at higher concentrations and result in the formation of a lyotropic liquid crystalline gel.²³⁴ Because of the chiral propeller-like conformation of the molecules, the columns have a dipole moment along their axes, which allows alignment and switching of the columns in the gel by an electric field.

Polar, water-soluble analogues **55** of these C₃-symmetrical molecules have also been studied, and they have been shown to form helical columns in a variety of polar solvents.^{235,236} A stepwise association process is observed when alcohol solutions of **55** are cooled. The molecules first polymerize into achiral columns with a small DP governed by their generic arene–arene interactions. Subsequently, these achiral columns become helical via a phase transition (Figure 30) and a strong growth spurt of the DP occurs, rendering a DP > 1000.²³⁷ During this transition, specific intermolecular hydrogen-bonding interactions occur that order the molecules in a helical fashion in addition to the arene–arene stacking. In water, the helicity of the columns is similarly lost at higher temperatures, but polymerization is maintained. Because of the increased strength of the arene–arene interactions and lower critical solution temperature (LCST) of the side-chains in water at higher temperature, long columns remain even at 90

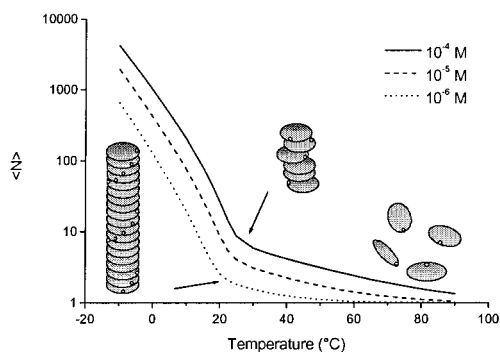


Figure 30. Average number of molecules **55**, $\langle N \rangle$, participating in one column in *n*-butanol at three different concentrations is given as a function of temperature. Arrows mark the transition from achiral to helical aggregates.

°C as proven by SANS. This stepwise growth of the columns shows great similarity to the self-assembly of the tobacco mosaic virus without the ribonucleic acid strand and will undoubtedly aid in the understanding of biopolymer self-assembly.²³⁸

In *n*-butanol the average distance between helix reversals in columns containing both **55a** and **55b** was found to exceed 400 molecules via “sergeant and soldiers”²⁰⁴ experiments. The high persistence length of the helicity results in strong (400-fold) amplification of chirality. In water, the helix inversions were found to occur after, on the average, every 12 disks, indicating that the helical order within the columns is highly solvent-dependent.²³⁶ In water, the solvent interferes with interactions accounting for helical order at all temperatures, resulting in a lower energy barrier for helix inversions.

VI. Supramolecular Coordination Polymers and Miscellaneous Systems

Metal coordination has been used to prepare a wide range of supramolecular complexes with geometries varying in complexity from simple cyclic dimers to catenanes, helicates, and cages with intricate geometries.²³⁹ In view of the apparent ease of construction of these well-defined assemblies, the number of 1-dimensional coordination polymers that has been characterized in solution is surprisingly small. There is extensive literature about coordination polymers in the solid state; this is outside the scope of the present review because these polymers do not exist outside the confinement of their crystal lattice. Most soluble coordination polymers, be they linear^{240–248} or hyperbranched,^{249,250} are held together by kinetically stable metal–ligand interactions and do not show the dynamic reversibility that is observed in true supramolecular polymers. Kinetically labile coordination complexes of metal ions such as Cu(I) and Ag(I) are required to form such aggregates. The first report of dynamic oligomers using these metals dates from 1992,²⁵¹ and it describes stereoregular coordination polymers using peptide-based polydentate ligand **56** containing thienyl, imidazolyl, and thioether donor sites (Figure 31).

The solid-state structure of the complex with silver triflate was determined with X-ray diffraction. On the

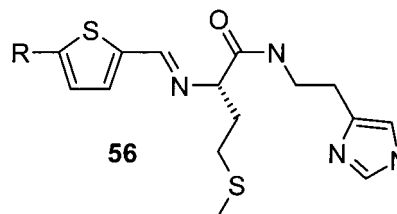


Figure 31. Peptide-based ligand **56** which forms reversible coordination polymers with Ag(I).

basis of a combination of vapor pressure osmometry and conductivity measurements in methanol, the average DP at 0.14 M concentration was estimated to be approximately 11. The reversibility of association was evident from the concentration dependence of the DP; at low concentrations only a monomeric complex was observed. Coordination complexes of Cu(I) and Ag(I) with phenanthroline ligands **57** have been used to prepare the first constitutionally well-defined coordination polymers from kinetically labile complexes in 1996.²⁵² It was demonstrated that high-molecular-mass polymers can be obtained from rigid bis(phenanthroline)ligand and Cu(I), if the solvent used cannot act as a competitive ligand for the metal (Figure 32).

The authors showed that ligand exchange takes place instantaneously in a mixture of Cu(I) and Ag(I) model complexes in coordinating solvents such as acetonitrile, whereas in 1,1,2,2-tetrachloroethane no evidence of ligand exchange was observed after several hours. The strategy to obtain the polymer was based on using the latter solvent, in which ligand exchange is slowed as much as possible. Upon titrating a solution of the monomer with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$, ¹H NMR spectra showed that end groups were present when less than 1 equiv copper salt had been added, and that at a 1:1 stoichiometry, only broad polymer resonances remained.²⁵³ The resulting solutions displayed high viscosities, indicating high molecular masses. Upon further addition of metal salt, the viscosity decreased again. From this experiment, it can be concluded that exchange between free and coordinated Cu(I) ions continues to occur, even in a noncoordinating solvent. When the polymer was precipitated and redissolved, no signs of degradation of the polymer were observed.

A different approach to coordination polymers has been taken by Terech and co-workers, who studied the aggregation of a Cu(II) tetraoctanoate (**58**, Figure 33). Using neutron scattering, it was shown that in apolar solvents the complex molecules assemble in a linear fashion to form threads with a cross section containing approximately 1 binuclear copper complex.²⁵⁴ Studies in Decalin²⁵⁵ have shown that under certain conditions, the rheological behavior of this system can be described by the theory of living polymers that has been developed by Cates and co-workers.^{256,257} It was suggested that, below a given transition temperature, physical junctions between chains act both as chain extenders and as efficient physical cross-links, resulting in rheological behavior that matches Cates' predictions of reversible polymers in the semidilute (entangled) regime. Above

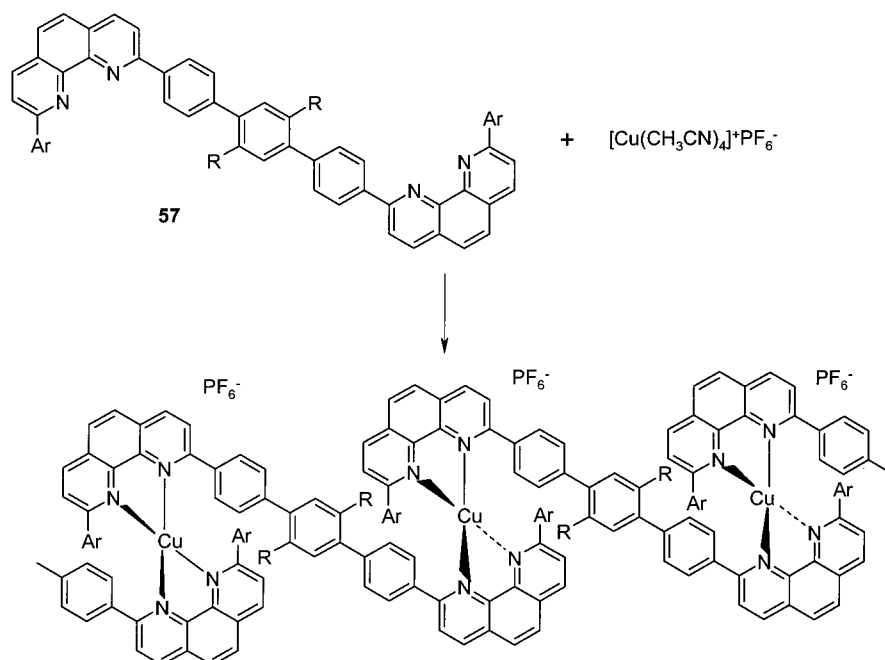


Figure 32. Bifunctional metal complexing **57** and its mode of polymerization upon addition of Cu^+ .

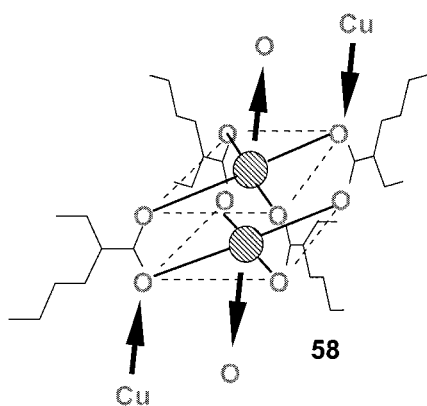


Figure 33. Mode of aggregation of $\text{Cu}(\text{II})$ tetraoctanoate **58** into linear polymers. (Reprinted with permission from ref 254. Copyright 1992 American Chemical Society.)

T_{trans} , these physical junctions melt, and the relatively short chains are no longer entangled.

Hunter and co-workers recently reported soluble, high-molecular-weight coordination polymers based on porphyrins.²⁵⁸ A porphyrin was provided with two pendant pyridine groups and a cobalt atom (which has six coordination sites) in the center. The bifunctional molecule **59** was anticipated to form coordination polymers in the fashion depicted in Figure 34. It was shown by ^1H NMR diffusion studies that polymeric aggregates were indeed obtained, and aggregation was confirmed by size exclusion chromatography, which showed that **59** forms aggregates which are significantly larger than those of **60**, which cannot associate beyond the dimeric state. Moreover, the size of the aggregate was shown to be dependent on the concentration of the solution. SEC was also used to show that the size of the aggregates could be tuned by addition of increasing amounts of monofunctional compound, incidentally demonstrating the reversibility of the aggregation process. Using the oligomer peaks in SEC that were observed upon

mixing **59** and **60** as calibration, the authors calculated that the aggregates in a 7 mM solution of **59** have an average molecular mass of 136 kDa, corresponding to a DP of about 100. These experiments nicely demonstrate the balance between kinetic stability (required for successful separation by SEC) and the reversibility needed for tuning the DP with monofunctional molecules.

Usually, ion–dipole interactions are insufficiently directional for the formation of linear supramolecular polymers because the functional groups providing the interaction tend to form clusters in such a system. Recently, Gibson and co-workers have shown that the combination of crown ethers and secondary ammonium ions can successfully be employed for this purpose.²⁵⁹ They designed a system based on Stoddart's finding that 24-dibenzocrown-8 and dibenzylammonium hexafluorophosphate associate strongly ($K_a = 2.7 \times 10^4$ in CDCl_3).²⁶⁰ Association of bifunctional molecules **61** and **62** was investigated by Gibson, and was shown to lead to chain extended aggregates (Figure 35), as was evident from the strong concentration dependence of the viscosity of 1:1 solutions of these compounds in $\text{CHCl}_3/\text{acetone}$. On the basis of end group analysis by NMR, the molecular weight of the aggregates was estimated to be 22 kDa for a 2 M solution, whereas at low concentrations the spectrum was dominated by signals of a cyclic dimer. Flexible films and fibers were obtained from concentrated equimolar solutions of **61** and **62**, from which it was inferred that entangled linear aggregates are present in the solid material. The same interaction between secondary ammonium groups and crown ether moieties has been used in dendritic self-assembly.²⁶¹

Li and McGown used the well-studied inclusion behavior of cyclodextrins to obtain nanotube aggregates of cyclodextrins (**63**) and diphenylhexatriene (**64**) (DPH).²⁶² These reversible, polymer-like aggregates can be formed because two phenyl "head-

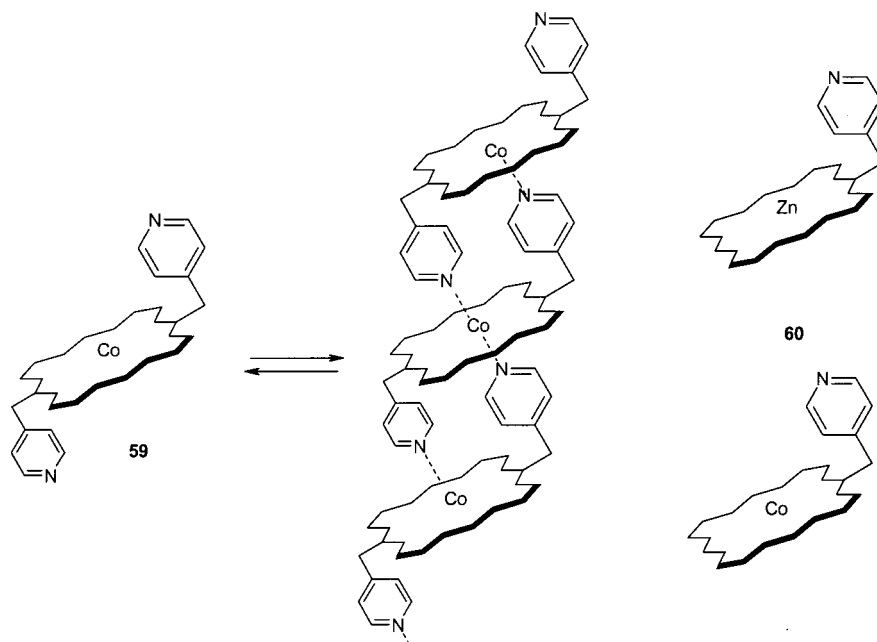


Figure 34. Formation of coordination polymers from porphyrin **59** and two chain stoppers **60**.

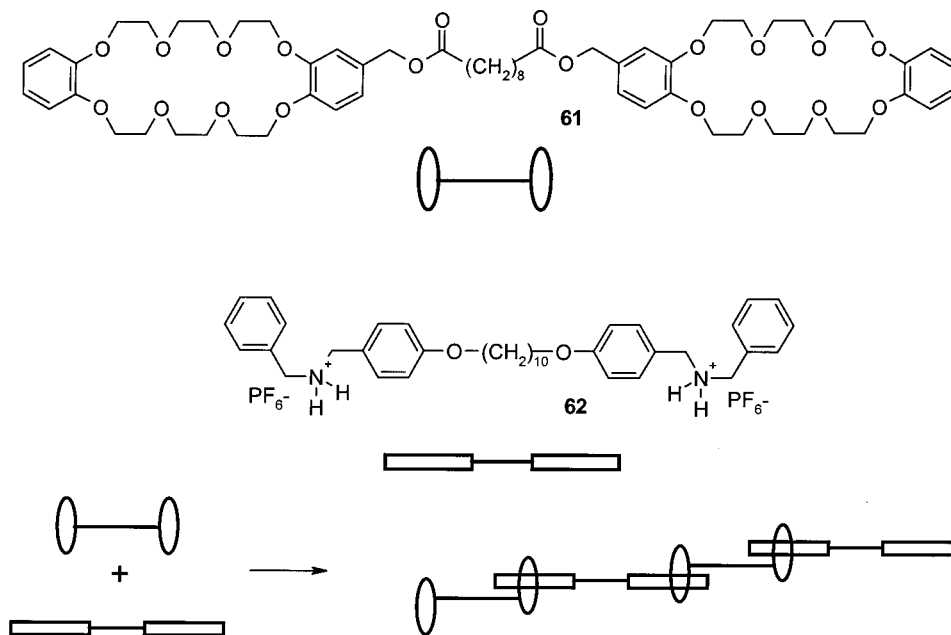


Figure 35. Polymerization via interactions between bifunctional ammonium compounds and bifunctional crown ether derivatives.

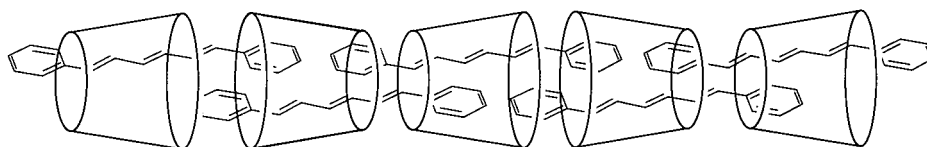


Figure 36. Supramolecular polymer consisting of β -cyclodextrin **63** and DPH **64**.

groups" of DPH fit into the cavity of β -cyclodextrin, and the cavity of γ -cyclodextrin can accommodate three phenyl groups. Binding of the phenyl groups of one DPH molecule in two different cyclodextrin cavities (Figure 36), results in polymeric aggregates with an estimated length of 20 β -cyclodextrins, or 20–35 γ -cyclodextrins, based on light scattering results. Scanning tunneling microscopy of the ag-

gregates on graphite confirmed their nanotube architecture.

The specific inclusion of adamantyl groups in β -cyclodextrin in aqueous environments has been used as binding interaction between adamantyl end-capped poly(ethylene oxide)^{263,264} or polyester and a cyclodextrin polymer. Even though the formation of linear chain extended structures was not specifically

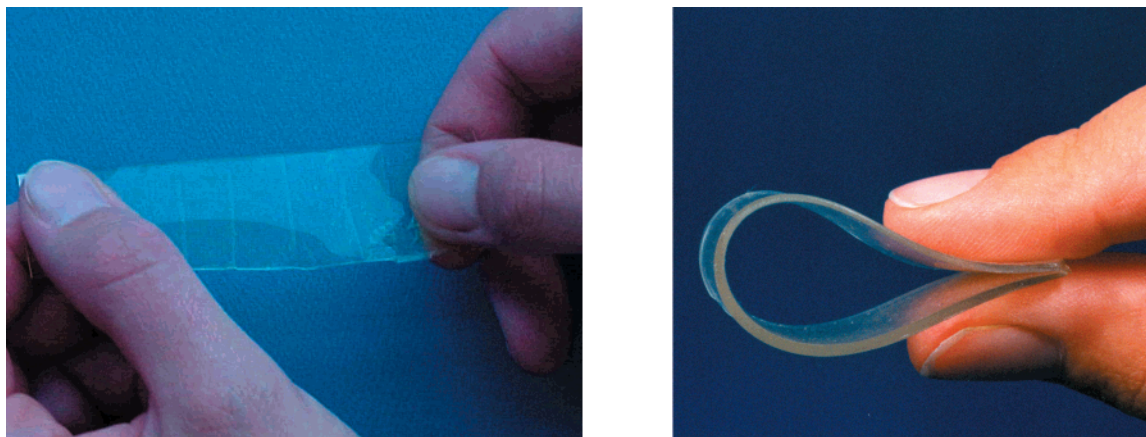


Figure 37. Supramolecular polymer materials created with the ureidopyrimidone unit. (Reprinted with permission from ref 118. Copyright 2000 John Wiley & Sons, Inc.)

studied – polyfunctionality of the cyclodextrin polymer gives rise to network architectures – the highly defined 1:1 stoichiometry of the interaction and its reversibility make this an interesting system. Interaction between the two polymers has been demonstrated through dynamic light scattering and viscosity measurements. The limiting value of the relaxation time in light scattering measurements (230 ms) was suggested to be related to the lifetime of the inclusion of adamantyl groups in the cyclodextrin cavity.

VII. Conclusions and Outlook

Roughly fifteen years after the first experiments toward supramolecular polymers (monomeric units held together by specific directional secondary interactions), it can be concluded that a new research area is added to the field of polymer science. The progress in supramolecular chemistry has paved the way to assembling small molecules into polymer arrays: structures that possess many of the well-known properties of “traditional” macromolecules. Because of the reversibility in the bonding, these supramolecular polymers are under thermodynamic equilibrium, and their properties can be adjusted by external stimuli. In this review we have analyzed three different classes of supramolecular polymers, in which hydrogen-bonded systems have been shown to be technologically relevant, having surpassed the state of being merely scientific curiosities. A large variety of applications is foreseen to be feasible, especially as this approach can also be used for the modification of telechelic oligomers or to modify existing polymers. But also, the possibility to tune the properties by simple copolymer formation due to just mixing monomers seems very attractive, whereas hybrids between blocks of macromolecules and supramolecular polymers are easy to prepare. Therefore, novel thermoplastic elastomers, superglues, hotmelts, and tunable polymeric materials are within reach (Figure 37).

Discotic molecules are of interest for their solution properties and their intriguing supramolecular architectures, in which a level of control in two-dimensional structures can be reached, that shows them to be of particular interest as models for natural systems. Their relatively poor mechanical properties,

such as low strength of the supramolecular gels and their phase transitions, gives them a low added-value with respect to covalent polymers as construction materials. However, their strong π - π interactions within a column lead to high electronic mobilities, a property that is essential in the development of plastic transistors and photovoltaics.^{265,266} Coordination polymers and a number of other approaches show the versatility of the supramolecular polymer approach.

Finally, an important conclusion that arises after discussing the literature on supramolecular polymers relates to the fact that these polymers are also interesting systems to be used by polymer theorists to verify a number of polymer theories. The thermodynamic nature of the supramolecular polymers enables the study of these systems without the kinetic constraints that are normally involved in the study of macromolecules. The future, however, will show the scope and limitations of this new field of supramolecular polymers. We foresee a bright future, and it is now clear that the status of supramolecular polymers has grown from scientific curiosities into systems with technological relevance.

VIII. Acknowledgments

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