

Invited Review

Polymeric Ordering by H-bonds. Mimicking Nature by Smart Building Blocks

Wolfgang H. Binder*

Institute of Applied Synthetic Chemistry, Vienna University of Technology,
A-1060 Wien, Austria

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Summary. Functional macromolecules can self assemble into regular structures yielding biological structures. The present review assembles recent literature on the formation of supramolecular polymers via hydrogen bonding forces and functional aggregates derived therefrom.

Keywords. Supramolecular polymer; Hydrogen bond; Macromolecules; Nanostructures.

Introduction

The organization of molecules forms the basis for structuring of living and non-living matter. Up to the 19th century covalent bonds were viewed as the sole basis of this process, the 20th century has put the noncovalent force in the limelight of this process. Together with the finding that large organic molecules (macromolecules such as proteins, peptides, nucleic acids, and oligosaccharides) together with small organic molecules (amino acids, lipids, carbohydrates, and others) are the basic structures of living matter, the interaction between molecules is determining in building up highly organized matter. Nature has found an easy mode of organizing the structural diversity within these molecules by so called “self assembly” processes (Fig. 1) [1]. Thus macromolecules are organized by intermolecular interactions (noncovalent forces), which drive the ordering process against the entropy-driven disordering process generating complex structures such as membranes (cells), *DNA*, connective tissue, or viruses.

Since life is a dynamic process, the structures themselves are dynamic, thus allowing the organization/reorganization of the biological structures. This gives biological structures (such as *DNA*, proteins, membranes) their unique evolutionary

* Corresponding author. E-mail: wbinder@mail.zserv.tuwien.ac.at

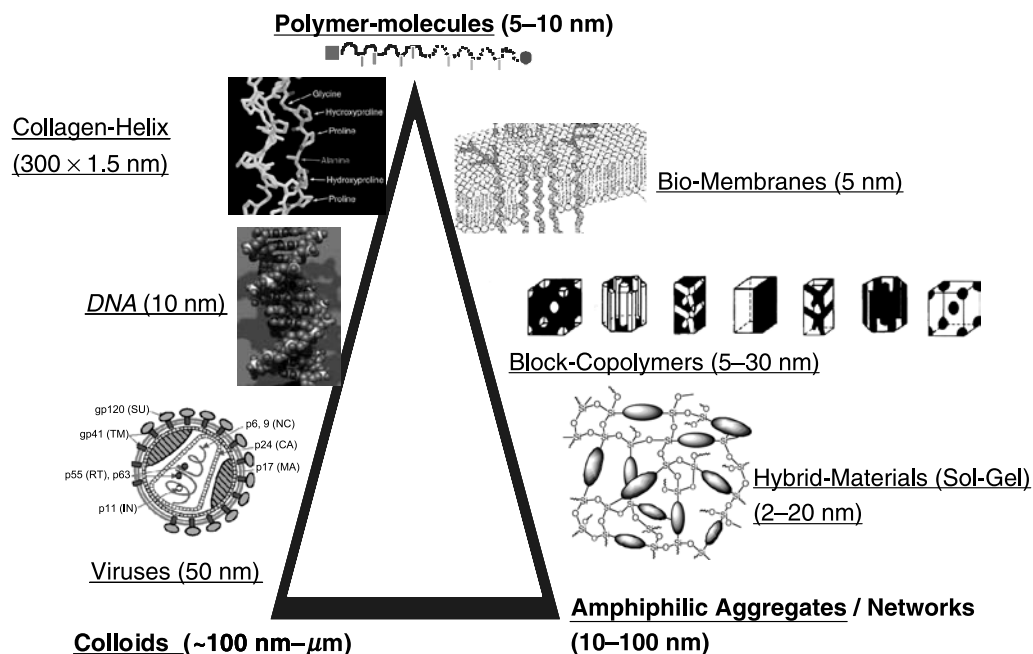


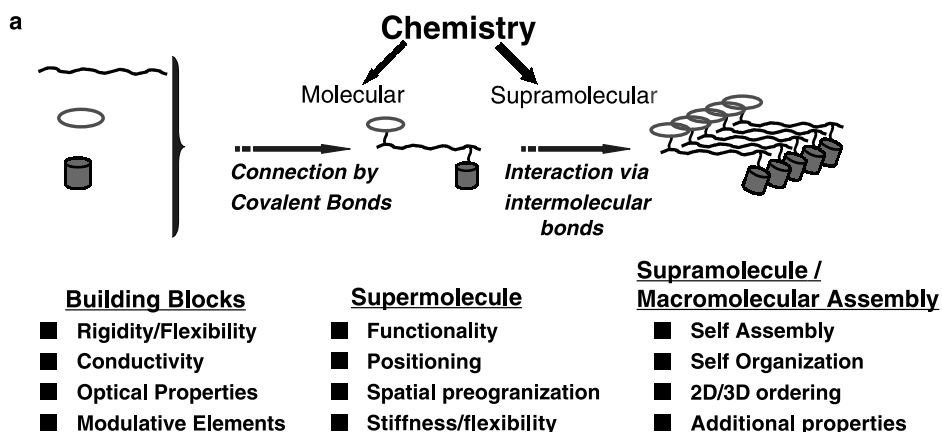
Fig. 1. Self assembly of macromolecules into ordered structures

properties. Two examples may illustrate the delicate balance between dynamic and static features mediated by noncovalent binding processes, where nature is permanently competing against the equilibrium-process:

- (a) *DNA*-replication is the basic evolutionary process of living matter. Critical for this process is the presence of a dynamic hydrogen-bonding pattern enabling the preservation of *DNA*-stability (and thus the genetic code) over many generations at temperatures below 40°C (*i.e.*, the average “working”-temperature of mammals), but allowing the fast strand-breaking prior to *DNA*-replication within the same temperature range mediated by replication enzymes. Small temperature changes (*i.e.*, heating to 60°C) leads to the reversible breaking of duplex-strands and the possibility to perform a PCR (polymerase chain reaction).
- (b) Membrane lipids assemble spontaneously into lipid-bilayer aggregates of defined molecular mobility under formation of cell-type entities (*i.e.*, liposomes) with thickness of 5 nm and size ranges of several microns. Hydrophobic interactions together with head-group interactions between the lipids can lead to a clustering of lipids (termed lipid rafts) [2], which mediate a variety of cellular functions such as receptor recognition, cholesterol transport, and viral entry. Membrane proteins are the central active moieties in membrane lipids, possible to exist only within the specific environment, which lipid membranes can provide as structuring assembly.

Due to the vast number of possible interactions between large molecules the understanding of this organizing force has formed an interdisciplinary field of research conducted by organic chemists, biochemists, polymer scientists, and

physicists. This has prompted the controlled buildup of organized structures built from synthetically functionalized molecules (so called supermolecules), which, by a self assembly process, generate supramolecules by interaction *via* noncovalent forces. *J. M. Lehn* [3] was the first to construct molecules for a specific organization and function (Fig. 2a). The principle relies on the controlled chemical synthesis of functional molecules (*supermolecules*), where specific intermolecular “binding sites” (*i.e.*, forces) are positioned at defined space-points within the molecule. Equally important is the introduction of flexibility or rigidity, since both – the noncovalent interaction as well as the degree of freedom – determine the final binding process. Usually the molecules used as building blocks are small, with molecular weights below 10000 Dalton. *Supramolecules* are then formed from these *supermolecules* by a self assembly process, where the sum of all forces together with the spatial distribution of all groups determines the aggregate. As



b ■ Ionic Forces

Crystal	~1000 kJ/mol	< 1 nm
Hydrated	100-250 kJ/mol	< 50 nm
Complex	250 kJ/mol	< 1 nm

■ Hydrogen Bonds

10-120 kJ/mol	0.15-0.20 nm / < 10 nm
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■ Hydrophobic Interactions

1-10 kJ/mol	< 20 nm
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■ Dipol/Dipol Forces

1-5 kJ/mol	< nm
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■ π - π Stacking

< 5 kJ/mol	< 0.5 nm
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■ Phase Separation Forces

5-30 nm

Fig. 2. (a) Principles of supramolecular chemistry; (b) Intermolecular ordering forces and their interaction energy and approximate range of action

in biology, the final structure can have an additional function in comparison to its “supramolecular building blocks”.

A variety of noncovalent forces can be used to direct the “supermolecules” into supramolecules (Fig. 2b): (a) ionic forces, often in the form of metal-complexes [4a]; (b) hydrogen bonds [4b, c]; (c) dipol–dipol forces [4d]; (d) π – π stacking interactions [5]; (e) hydrophobic interactions [6]; and (f) steric stabilization forces [7]. Important for the molecular design is the absolute energy of the respective interaction together with its length of interaction. Additionally some forces are directed (hydrogen bonds, dipol–dipol forces, π – π stacking) whereas others are uniform (ionic forces, hydrophobic interaction, and steric stabilization). This allows the buildup of molecular arrays by directed, complementing forces as well as the formation of isotropic, nondirected assemblies [8].

Similar to small supermolecules (such as crown ethers, cryptands, calixarenes, or rotaxanes) synthetic macromolecules are among the most important molecules for this organizational process. With respect to their molecular dimension they are on the upper range of size (1–10 nm), which is unreachable for small molecules with molecular weights below 1000 Dalton. Additionally, in contrast to small molecules, macromolecules allow the controlled buildup of molecular architecture and the design of additional ordering forces due to the immiscibility of polymer chains [9]. Thus block copolymers (diblock, A–B–A triblock, or multiblock copolymers) as well as polymers with complex architectures (star and star-block copolymers) can be tailored with defined composition and functionalization.

Hydrogen bonding interactions are among the most important structuring forces in supramolecular chemistry, offering the tuning of forces starting from several kJ/mol up to more than 80 kJ/mol. The binding force of multiple hydrogen

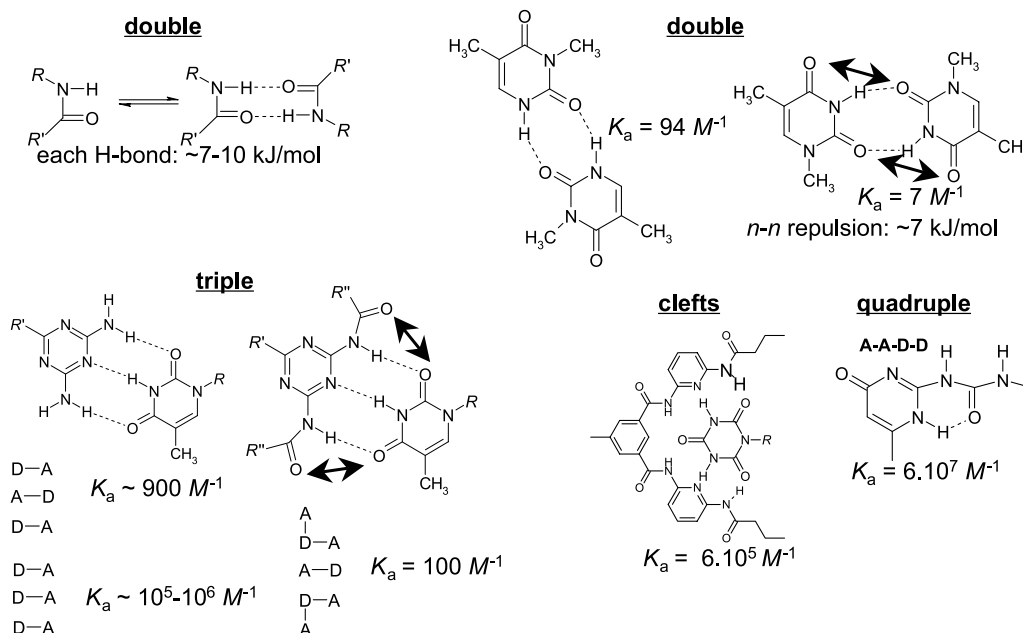


Fig. 3. Hydrogen bonds and their association constants (A: Hydrogen bonding acceptor; D: Hydrogen bonding donor; n : lone pair repulsion)

bonding systems can be tuned leading to association constants from several M^{-1} up to more than $100000 M^{-1}$. The binding strength is influenced by the number of hydrogen bonding interactions [10] (each bond contributing about 7.9 kJ/mol) as well as other effects such as (a) secondary repulsion [10b–d]; (b) electronic effects [11]; (c) preorganisational effects [12]; and (d) tautomeric effects [13]. (Details of evaluating the binding strength of hydrogen bonds can be found at *Schneider et al.* [14] and *Rotello et al.* [10a].) An important advantage of hydrogen bonds over other intermolecular interactions is the sequential type ordering due to the complementing nature of specific hydrogen bonds which allows directed ordering into alternating sheets and three-dimensional objects. The use of macromolecules in the organization of supramolecular structures (“supramolecular polymers” in the widest sense) allows the buildup of new functional materials, where the properties of macromolecules are ordered *via* hydrogen bonding forces (Fig. 4). Thus linear structures can be built according to *Lehn et al.* [15] by the association of bivalent building blocks (Fig. 4a), higher organized networks by use of three dimensional building blocks (Fig. 4b). Networks with looser structure (*i.e.*, those shown in Fig. 4c) allow the formation of soft networks with few, but defined numbers of crosslinking points. In all cases, the molecular properties of the building blocks

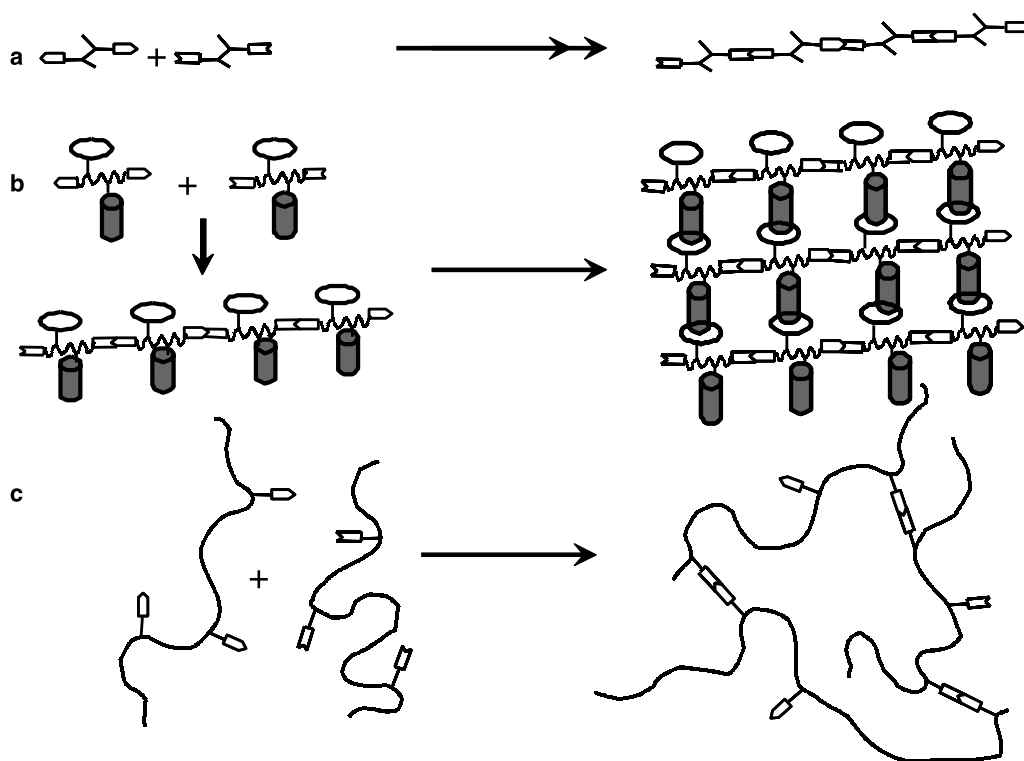


Fig. 4. (a) Formation of linear polymers from bivalent associative building blocks; building blocks with complementing hydrogen bonds of sufficient strength assemble into linear “polymers” with molecular weights in dependence of the binding constant; (b) 2-dimensional and 3-dimensional network formation using multiple complementing sites using the same principle as in (a); (c) Building of network structures from polymer chains bearing low amounts of hydrogen bonds

(*i.e.*, hardness, flexibility, conductivity, optical emission properties) can be combined and lead to the formation of new materials' properties. Thus, the concept of biological ordering is combined with modern polymer chemistry, introducing the dynamic ordering process into synthetic macromolecules.

Since a variety of reviews [16] has covered the general topic of supramolecular polymers recently, the present review assembles concepts for the assembly of macromolecules and nanoparticles into regular structures by use of hydrogen bonding systems. Literature from the past ten years is covered, aligning a focus on most recent publications, where significant effects have been achieved in terms of materials' effects and materials' properties *via* hydrogen bonding systems.

Polymeric Networks

The first designed supramolecular polymer was introduced by *Stadler et al.* [17] by transforming a linear, noncrosslinked soft polybutadiene chain into a thermoelastic elastomer (Fig. 1b). The concept relied on the statistical introduction of hydrogen bonds into the polybutadiene by use of an ene-type reaction, thus creating noncovalent crosslinking sites between the polymer chains. It was found that a hydrogen binding donor-acceptor unit for each 50 butadiene-units (*i.e.*, at 2 mol%) is sufficient to drastically change the thermal and mechanical properties of the material, thus demonstrating that a couple of weak bonds on side of a polymer chain can be a very efficient crosslinking structure.

The resulting thermoreversible network displays elastic and thermoelastic properties, due to the formation of domains within the polymer consisting of aggregated domains of associated polymer-chains dispersed within the residual polymeric matrix. Rheological thickening-effects are observed in solution, where the increased crosslinking density leads to non-*Newtonian* behavior. The reversibility of the hydrogen bond at higher temperature or at increased stress onto the material leads to tunable behavior within small temperature intervals. The concept has been applied to many polymers such as poly(butadienes) [18], poly(isobutylenes) [19], and poly(siloxanes) [18]. The extension of the concept using different types of hydrogen bonds has been demonstrated in other systems: *i.e.*, triazine – barbituric acid in the case of poly(propylene) [20]; simple –OH bond clusters in the case of

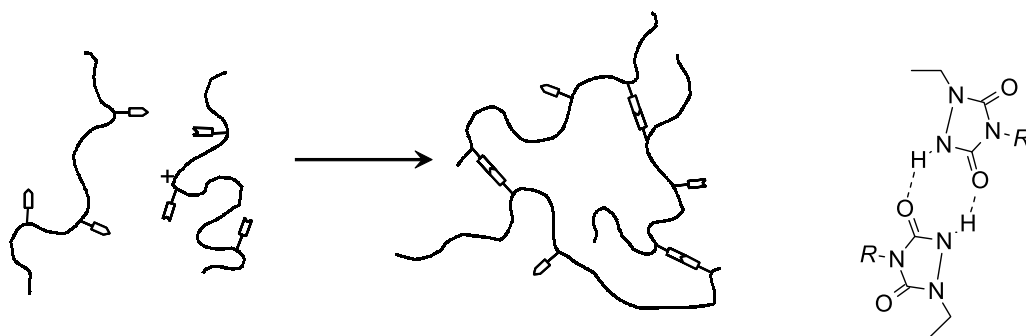


Fig. 5. Ordering of flexible polymer chains (*i.e.*, poly(butadiene) by uradiazole-hydrogen bonds into networks)

poly(butadiene) [21]; 2-ureido-4[1H]-pyrimidinone clusters in poly(olefines) [22], as well as melamine/imide clusters in poly(tetrahydrofurane) [23].

Materials and Surfaces by 2-Ureido-4[1H]-pyrimidinone as Connecting Unit

The association of small building blocks leading to materials with polymeric properties in solution (see Fig. 4a) is restricted by the strength of the binding constant: as calculated by *Meijer et al.* [24] a binding constant at $10000 M^{-1}$ leads to an aggregation number of about 100 molecules at a concentration of the building blocks at $1 M$. In order to reach a sufficient virtual chain length, an association constant of more than $10000 M^{-1}$ is advisable. Thus the 2-ureido-4[1H]-pyrimidinone unit [25] (and related units such as the ureidotriazine-unit [26], Fig. 6) were developed featuring a binding constant of $6 \cdot 10^7 M^{-1}$, leading to a very strong association of the building blocks. This in turn leads to materials approaching the properties of pure polymers [27], but with a stronger temperature dependent behavior allowing to organize a broad variety of different materials leading to thermoplastic [28], elastomeric [29], conductive [30], and new optical behavior [31]. Additional solvophobic interactions between the hydrogen bonding interactions can lead to helix formation [32] including chiral elements [33]. Association of block copolymers has been described by *Long et al.* [34] investigating the effects of phase separation in relation to hydrogen bonding effects.

Two recent examples illustrate the applicability of these strong hydrogen bonding interaction *via* (a) phase separation processes and (b) induction of surface roughness by noncovalent hydrogen bonds.

- (a) Polymerization induced phase separation (PIPS) within hydrogen bonded polymeric fragments can lead to materials with combined properties and defined morphology. *Keizer et al.* [35] (Fig. 7) have described the formation of “droplets” within an acrylate matrix using a miscible supramolecular polymer bearing associative endgroups. The miscibility is reduced during the polymerization reaction of the acrylate, thus leading to finely dispersed droplets of the supramolecular polymer within the bulk-polymer matrix. The size of the droplets can be varied starting with less than 100 nm up to several microns in diameter.

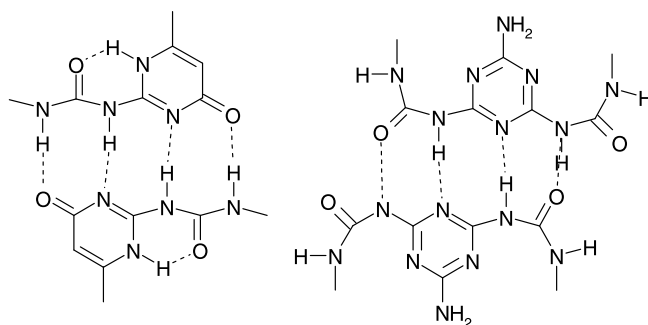


Fig. 6. Quadruple hydrogen bonds with binding constants of $6 \cdot 10^7 M^{-1}$ and $2 \cdot 10^4 M^{-1}$

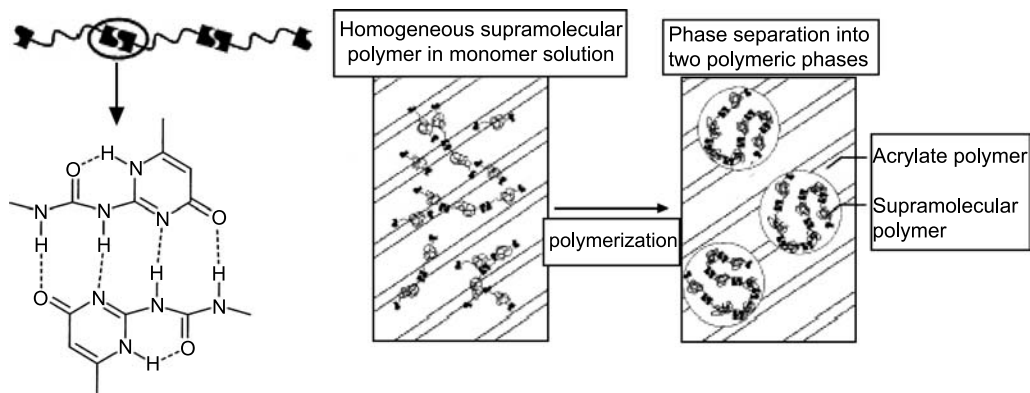


Fig. 7. The monomeric building blocks can self assemble into ordered structures by use of quadruple hydrogen bonds; starting from a homogeneous polymer and a monomer solution, the polymerization of the monomer (an acrylate) is started; during the course of the polymerization, phase separation takes place and leads to droplet formation; the droplet size can be tuned by variation of the crosslinker within the polymeric matrix; reprinted with permission of Ref. [35]

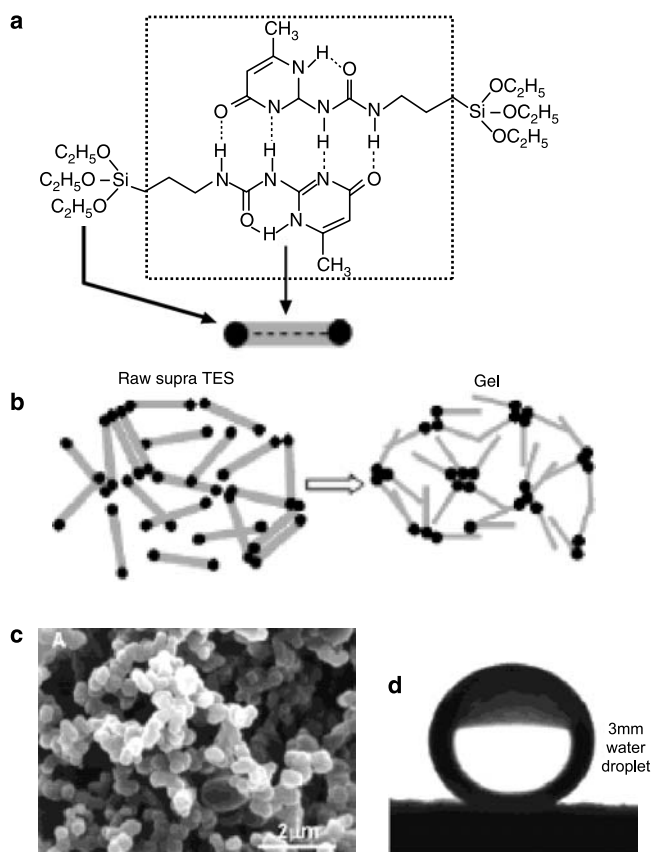


Fig. 8. (a) The supramolecular associate (held together by quadruple hydrogen bonds) is subjected to a sol-gel crosslinking in aqueous media; (b) During crosslinking of the Si-alkoxides, phase separation is taking place – (c) leading to a surface with a corrugated structure; (d) The surface displays superhydrophobic behavior, leading to the formation of water droplets with a contact angle above 150° ; reprinted with permission of Ref. [36]

- (b) Defined surface roughness can be induced by hydrogen-bonding systems bearing trialkoxy-siloxane units (Fig. 8) [36]. The hydrogen-bonded associate is subjected to a sol-gel mediated crosslinking process of the siloxane units, leading to a three dimensional network. Phase separation processes lead to the formation of defined granules and holes on the surface. The material displays a defined surface roughness and thus superhydrophobic contact angles in contact with water, mimicking the self-cleaning properties of the lotus-leaf [37]. Thus the noncovalent preorganisation on basis of the hydrogen bonds leads to phase effects not reachable with conventional polymer systems and presents a biomimetic approach to a highly sophisticated, bioinspired material.

Phase Separation Effects in A–B Systems

One of the disadvantages of the hydrogen bonds mentioned in the sections above is the A–A type interaction, preventing the stacking of two or more different macromolecules in sheets and nanostructured materials due to the self-complementarity of the hydrogen bonds used. Most macromolecules are nonmiscible in the solid state as well as in concentrated solution. If two or more blocks of macromolecules are linked by a covalent bond, the immiscibility of the individual blocks leads to microphase separation, visible as regions of phase separated domains (size about 5–50 nm, depending on the individual length of the macromolecules) of individual polymers (see Fig. 9) [38].

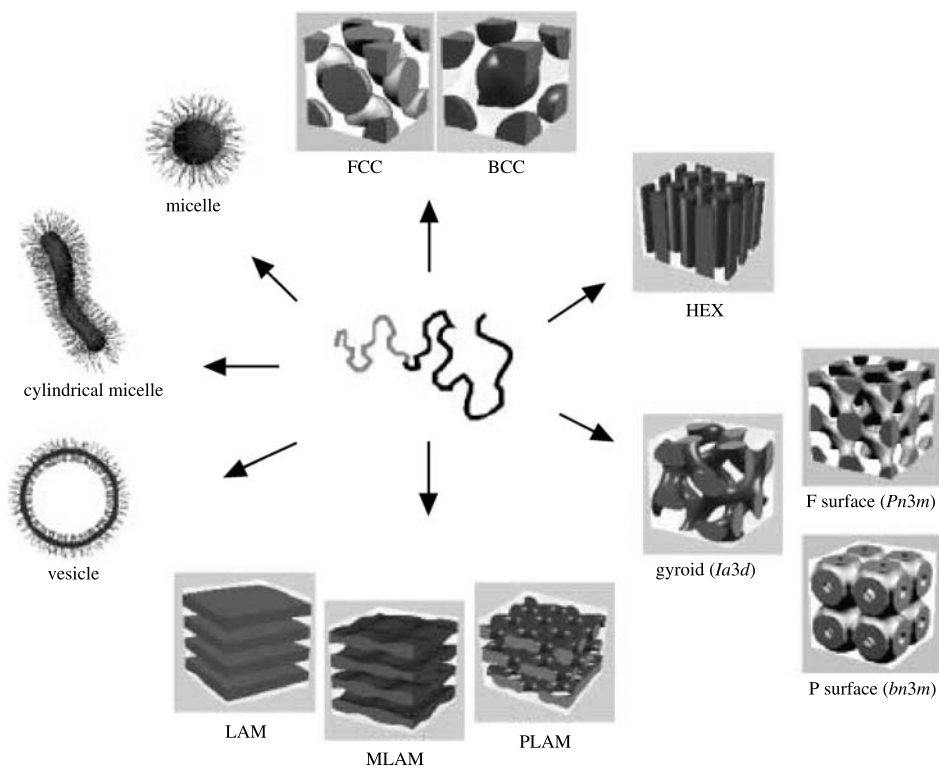


Fig. 9. The organization of block-copolymers by phase separation into regularly ordered structures with sizes in the \sim nm regime; reprinted with permission of Ref. [38]

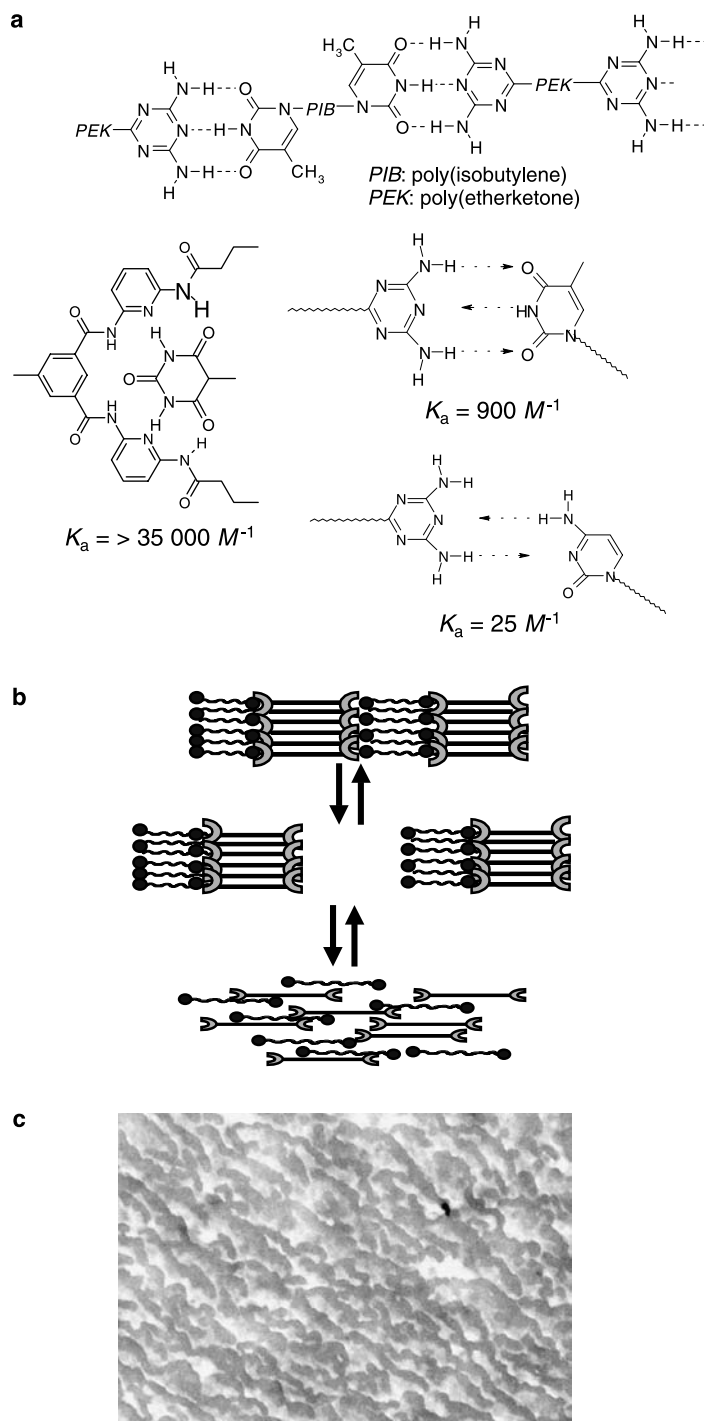


Fig. 10. (a) Two different polymers (*PEK* and *PIB*) bearing complementary hydrogen bonds order into ordered structures depending on the strength of the hydrogen bond; (b) The ordering is reversible (*i.e.*, by increasing the temperature); (c) TEM-picture of the material consisting of alternating layers of *PEK* and *PIB* polymer; reprinted with permission of Ref. [39a]

Hydrogen bonding systems using the A–B type interaction can be used to force immiscible polymers into regular order within sheets consisting of alternating polymers bearing the appropriate endgroup (Fig. 10) [39]. Two types of polymers were investigated, namely poly(etherketones) and poly(isobutylenes), both absolutely immiscible polymers in the solid state. The strength of the hydrogen bonds affixed to the polymers was found to be essential in overcoming the phase separation force present within them: Stronger hydrogen bonds (binding constants $\sim 1000 M^{-1}$ and $30000 M^{-1}$) lead to the formation of regular arrays of alternating polymers, whereas weak hydrogen bonds (with a binding constant of $\sim 25 M^{-1}$) still lead to immiscibility (visible by the rough and unordered structure). Important is the reversibility of the process, which can be induced by temperature mediated

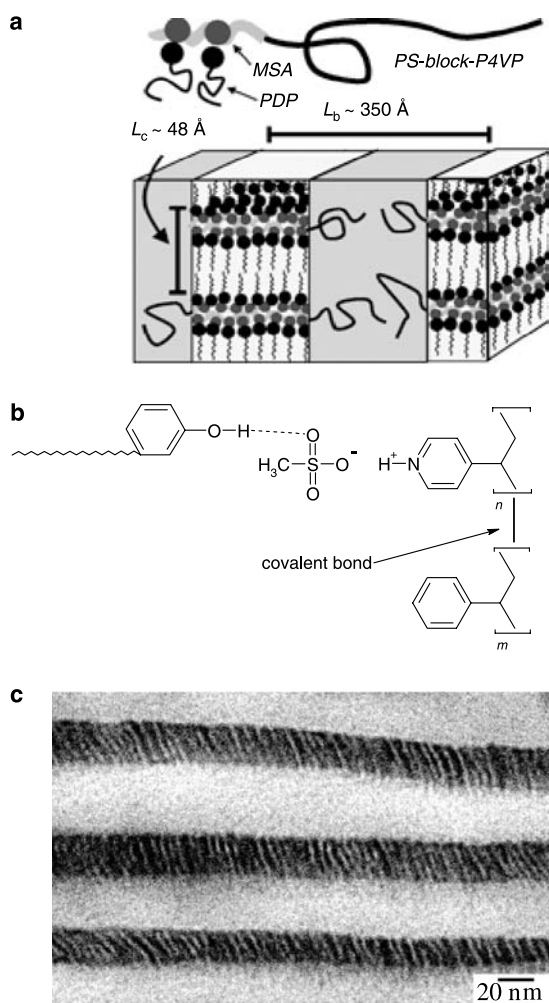


Fig. 11. (a) Sheet formation of a block copolymer consisting of poly(styrene)-block-poly(4-vinyl)pyridine; (b) Structure of the block copolymer: the alkyl-sulfonate sidechains bridge the pyridine blocks and the phenol by use of a hydrogen bond; (c) TEM-picture of the sheet formation; the size bar is 20 nm; reprinted with permission of Ref. [41]

breaking of the bonds: Bonds with binding constants of $\sim 1000 M^{-1}$ are reversibly destroyed up to temperature below the glass transition temperature, whereas the regular structure is still retained in the case of the strong hydrogen bond [40]. This allows the design of materials with tunable and modulative material properties.

A similar system has been reported for side-chain functionalized polymers bearing single hydrogen bonds (Fig. 11) [41]. A large number of hydrogen bonds can be affixed, leading to a cooperative behavior between the attached sidechains and the basic polymer chain. Hydrophobic alkyl-chains can thus be noncovalently bound to the polymer-backbone, leading to microphase separation of the polymer.

Domains, consisting of alternating sheets of the polymer and the noncovalently bound chains are formed, leading to materials with nanometer-sized layers and tubules. The domain-size can be tailored by variation of the polymer-chain length as well as the length of the alkyl-chain. The important point is the reversibility of the hydrogen bond, which can be cleaved at elevated temperatures: The phase-state changes at a temperature above the dissociation temperature (*i.e.*, where the alkyl-side-chains are cleaved off) leading to a modulation of the pattern or its (reversible) destruction [42]. The resulting materials thus show drastic changes of physical properties at the critical temperature of the cooperative dissociation process. As demonstrated by *ten Brinke et al.* [43] the conductivity as well as the optical reflectivity can be tuned reversibly by use of this organizational principle.

Connecting Nanoparticles and Polymers by Hydrogen Bonds

Equally important to polymeric networks (*i.e.*, networks and assemblies consisting entirely of macromolecules) is the incorporation of nanoparticles by use of non-covalent interactions (Fig. 12). Hydrogen bonding interaction can be used to assemble metal (*i.e.*, Au, *POSS*) nanoparticles into polymeric matrices. The size of the nanoparticles usually is small (gold nanoparticles ranging from several nm to 20 nm, *POSS*-nanoparticles having a size of 1.5 nm). There are two important issues: (a) The selective binding of nanoparticles onto (block-co)polymers and (b) the binding of nanoparticles onto polymeric surfaces. In both cases, a selective functionalization of the respective structures is to be achieved. *Rotello et al.* [44] have focussed on the thymine/2,6-diaminopyridine system to achieve selective binding between nanoparticles and polymers (Fig. 12). A sidechain modified block-copolymer (consisting of polystyrene) can be selectively modified with 2,6-diamino-1,3,5-triazine or 2,6-diaminopyridine units. Gold-nanoparticles (accessible via reduction of $AuCl_3$ in controllable size) can be modified *via* a self assembled monolayer and subsequently thymine-moieties can be attached. The nanoparticles interact selectively with the functional block by the complementing hydrogen bonding interaction. Similarly, the functional nanoparticles can act as crosslinkers for these sidechain functionalized polymers [45]. This generates modulative gels, whose aggregation can be triggered by small temperature changes breaking the hydrogen bonding interaction. This concept has also been applied to the selective binding of nanoparticles to specific regions of a patterned surface [46] as well as to the reversible aggregation of nanoparticles and dendrimers [47]. The modulative properties of the hydrogen bonding interaction can be used to

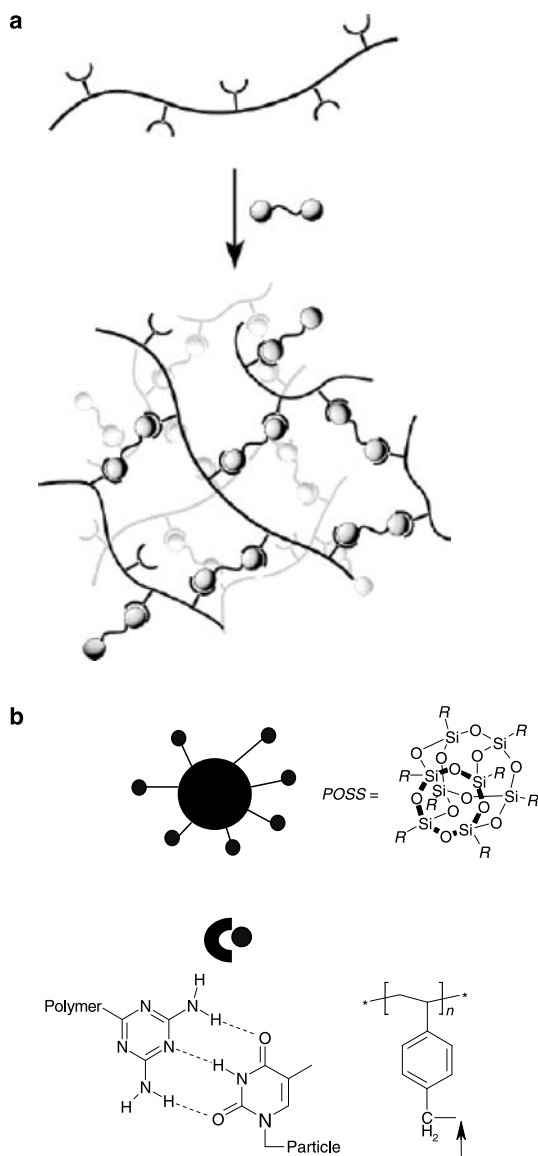


Fig. 12. (a) Binding of functionalized nanoparticles onto the sidechain of a polymer *via* specific hydrogen bonding; (b) Functionalized particles (*POSS*, Au) and the specific hydrogen bonding interaction; reprinted with permission of Ref. [45d]

effect changes in electrochemical potentials [48], spacing between nanoparticle-polymer clusters [49], as well as shrink/enlarge the size of polymersomes [50].

Miscellaneous Assemblies

A variety of hydrogen-bonded polymeric assemblies has been reported using various hydrogen bonds. The association of disc-like building blocks can be achieved using multiple hydrogen bonds on a central, disc-shaped aromatic core (Fig. 13a) [51]. Hexagonal columnar structures are formed, which can be stabilized by

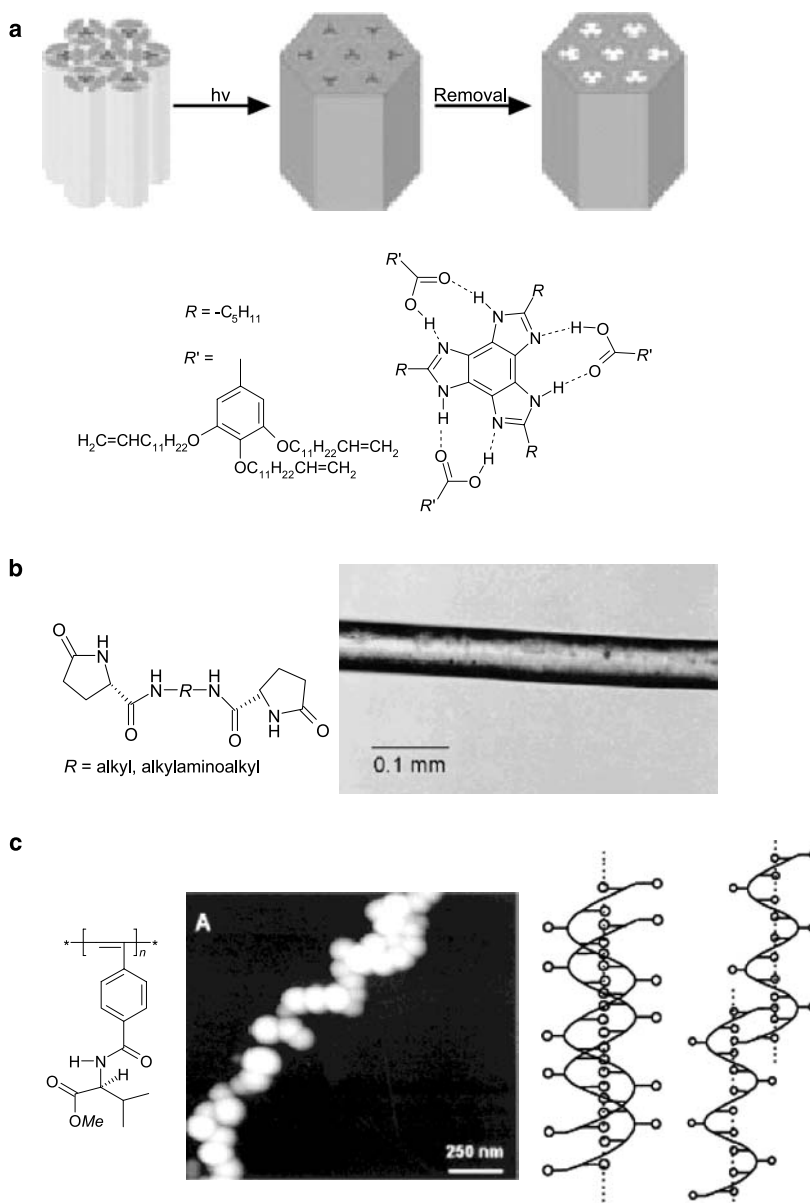


Fig. 13. (a) Formation of hollow channels after self-assembly and polymerization of the double bonds; the inner core is removed afterwards leaving behind the nanoporous structure; reprinted with permission of Ref. [51]; (b) Fiber formation by self-organization; reprinted with permission of Ref. [53]; (c) Formation of helices from *L*-valine-substituted poly(acetylene) (scale bar: 250 nm); reprinted with permission of Ref. [54]

subsequent polymerization of the terminal acrylate moieties. The central core can subsequently be removed due to the noncovalent bonding between the crosslinked stacks and the central core, leading to nanoporous structures of defined geometry. Thus the dynamic nature of the hydrogen bond is efficiently used to generate hollow objects.

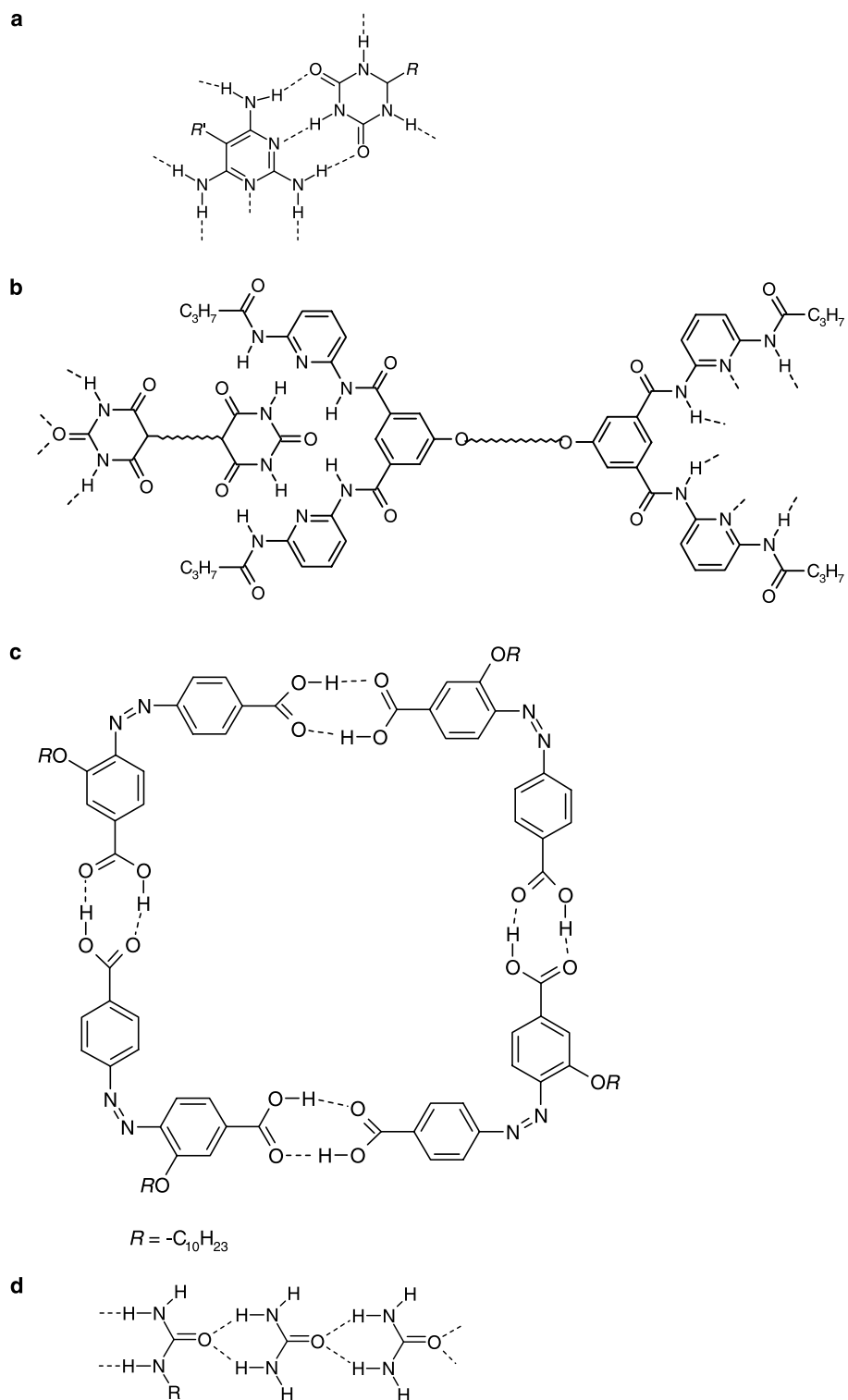


Fig. 14. (a) Formation sheets and strands via the 2,4,6-triaminopyrimidine/barbituric acid interaction; (b) Fiber formation by cleft-type hydrogen bonds; (c) Formation of switchable aggregates modulative via UV-irradiation by *cis/trans* isomerization of the diazo-bond; (d) Supramolecular polymers by the association of ureas

A highly cooperative assembly of multiple hydrogen bonds into noncovalent gels [52] has been presented by *Mathias et al.* [53] (Fig. 13b) reporting on the assembly of pyroglutamic acids into gels. The association of complementing, singular hydrogen bonds leads to the formation of fibers (with diameters of 0.05 mm!) in solution, which subsequently associate into an ordered gel. The gel is stable up to temperatures of 200°C in organic solutions, but can be broken upon addition of small amounts of water. The formation of artificial helices on basis of assembling polymers has been described by use of poly(acetylenes) bearing pendant *L*-valine sidechains [54]. Two effects are important for the association of these ladder-type polymers into double-stranded helices: (a) The reduction of conformational freedom by the poly(acetylene) chain with respect to a conventional alkyl-chain and (b) the selective association of the *L*-valine residues by specific hydrogen bonding. An AFM-image of the associates on a flat surface demonstrates the presence of a string-pearl structure reminiscent of natural *DNA*.

Figure 14 provides an additional overview on other hydrogen-bonding interaction useful for the organization of molecules into regular arrays and structures. *Lehn et al.* [55] and others [56] have reported on the formation of aggregates on basis of 2,4,6-triaminopyrimidine/barbituric acid. The formation of regular strands and sheets due to the multiple hydrogen bonding sites is possible in this case. Related systems (Fig. 14b) lead to the formation of fibers [57]. Azo-dibenzoic acid can be assembled onto quadrangles, if the nitrogen-bond is in the *cis*-configuration (Fig. 14c) [58]. In this case, the quadrangles can stack over each other to form regular stacks and bundles when deposited onto surfaces. The photoinduced switching between the *cis-trans* isomers of the diazo-bond leads to the complete suppression of the association due to steric reasons. This systems represents a photomodulative aggregate, where the steric preorganisation of the hydrogen bonds can be used to induce or suppress the formation of large aggregates. A very simple example of the association of small building blocks into supramolecular polymeric aggregates has been demonstrated by *Bouteiller et al.* [59]. Ureas and the related bis-urea derivatives assemble in organic solvents into polymers with relatively high (“virtual”) degrees of polymerization. The structures are not only stabilized by the relatively strong hydrogen bond ($K_{\text{ass}} = 1 \cdot 10^5 M^{-1}$) but also by hydrophobic interactions mediated by the substituents at the urea-structure.

Concluding Remarks

The preceding review has assembled recent literature on supramolecular polymers, where hydrogen bonds form the structurally directing force for their organization. Research in this area is quite well developed, and offers a variety of concepts to organized small molecules, polymers, and nanoparticles into regular structures exerting a specific 2D- or 3D structure. Due to the diverse nature of polymers, which allows to introduce specific functionality (*i.e.*, mechanical properties, chemical resistance, optical emission, electrical conductivity, and -semiconductivity) the way is open to construct function into the newly formed materials. As demonstrated in this review, the basis for future developments is already laid to generate tailored materials with modulative features (featuring the combination of properties

and their easy modulation by external stimuli) by taking advantage of the reversible and directed features of hydrogen bonding assemblies.

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