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VIEWPOINT

# Functional Materials Based on Self-Assembly of Polymeric Supramolecules

**Olli Ikkala[1]* and Gerrit ten Brinke[1,2]***

**Self-assembly of polymeric supramolecules is a powerful tool for producing functional materials that combine several properties and may respond to external conditions. We illustrate the concept using a comb-shaped architecture. Examples include the hexagonal self-organization of conjugated conducting polymers and the polarized luminance in solid-state films of rodlike polymers obtained by removing the hydrogen-bonded side chains from the aligned thermotropic smectic phase. Hierarchically structured materials obtained by applying different self-organization and recognition principles and directed assembly form a basis for tunable nanoporous materials, smart membranes, preparation of nano-objects, and anisotropic properties, such as proton conductivity.**

Recently there has been much effort to develop novel concepts for preparing structures and objects approaching the molecular level. Electronics miniaturization provides a strong motivation because present-day lithography faces fundamental problems in achieving further reduction in feature sizes by orders of magnitude. For example, molecular-level switching elements based on interlocking rings and their use in memory elements in electronics have been studied by the groups of Stoddart and Heath (*1*).

There have also been attempts not only to construct individual nanoscale functional features but also to control bulk materials structures, defects, and anisotropy at all length scales from the macroscopic scale down to the molecular level. Very recently, it was demonstrated that if sufficiently high-quality single crystals can be grown by vapor deposition, even organic oligomers can have high charge-carrier mobilities, as well as showing lasing and luminance (*2*). In polymers, spin-cast self-organized polyalkylthiophenes have recently been shown to have enhanced charge-carrier mobility (*3*) and even superconductivity (*4*). However, although self-organization allows high structural control at the local length scale, the inherent tendency for coiling of polyalkylthiophenes causes folds, as visualized by Bäuerle *et al.* (*5*). In such polymers, it may be fundamentally difficult to achieve a monodomain-like structure with high overall order.

Here, we describe some possibilities for preparing functional polymeric materials using the "bottom-up" route, based on self-assembly of polymeric supramolecules. Directed assembly leads to the control of structure at several length scales and anisotropic properties. The physical bonds within the supramolecules allow controlled cleavage of selected constituents. The techniques constitute a general platform for constructing materials that combine several properties that can be tuned separately.

To achieve enhanced functionalities, the principal periodicity is at ~10 to 2000 Å. There are established ways to accomplish this by using various architectures of block copolymers (*6*), in which the structure formation is based on self-organization (*7*), that is, on the repulsion between the chemically connected blocks. Depending on the architecture, block length, and temperature, it is possible to obtain lamellar, cylindrical, spherical, gyroid, or more complicated structures in the 100 to 2000 Å range. Also, rodlike moieties within the block copolymers can be used (*7*, *8*) to further tailor the structures in terms of shape persistency. However, self-organization renders only the local structures. To fully realize the opportunities offered by the symmetry of the self-organized structures to prepare materials with a strongly directional variation of properties, additional mechanisms and interactions have to be invoked to obtain macroscale order. This may be achieved by flow, by electric or magnetic fields, or by using topographically patterned surfaces (*9*–*12*). One can further extend the structural complexity by mixing block copolymers with additional polymers and inorganic additives, thereby increasing the self-organization periods into the photonic band gap regime (*13*). Block copolymers have also been used as templates for the synthesis of inorganic materials, even allowing the creation of separate ceramic nano-objects (*14*).

To achieve even greater structural complexity and functionality, we can combine recognition with self-organization. Lehn elaborated on the concept of recognition in synthetic materials, whereby two molecules with molecularly matching complementary interactions and shapes recognize each other and form a receptor-substrate supramolecule (*15*). To achieve sufficient bonding, synergism of several physical interactions is often required. Homopoly-

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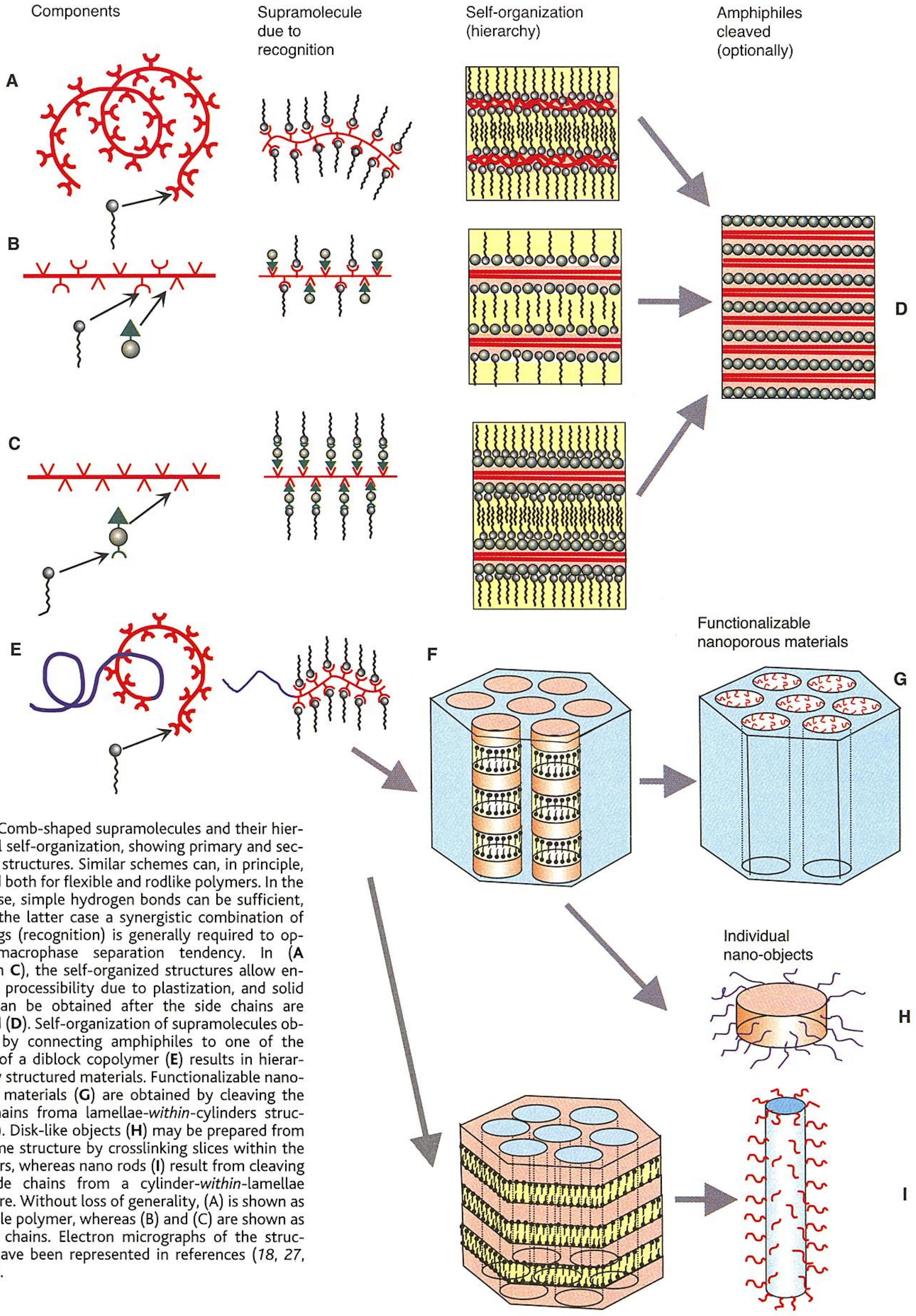

**Fig. 1.** Comb-shaped supramolecules and their hierarchical self-organization, showing primary and secondary structures. Similar schemes can, in principle, be used both for flexible and rodlike polymers. In the first case, simple hydrogen bonds can be sufficient, but in the latter case a synergistic combination of bondings (recognition) is generally required to oppose macrophase separation tendency. In (**A** through **C**), the self-organized structures allow enhanced processibility due to plastization, and solid films can be obtained after the side chains are cleaved (**D**). Self-organization of supramolecules obtained by connecting amphiphiles to one of the blocks of a diblock copolymer (**E**) results in hierarchically structured materials. Functionalizable nanoporous materials (**G**) are obtained by cleaving the side chains froma lamellae-*within*-cylinders structure (**F**). Disk-like objects (**H**) may be prepared from the same structure by crosslinking slices within the cylinders, whereas nano rods (**I**) result from cleaving the side chains from a cylinder-*within*-lamellae structure. Without loss of generality, (A) is shown as a flexible polymer, whereas (B) and (C) are shown as rodlike chains. Electron micrographs of the structures have been represented in references (*18*, *27*, *30*, *31*).

merlike supramolecules have been constructed based on a combination of four hydrogen bonds (*16*) and through coordination (*17*). Supramolecules can spontaneously assemble or self-organize to form larger structures (*15*).

A general framework for forming complex functional materials emerges. Molecules are constructed that recognize each other in a designed way. The subsequent supramolecules in turn form assemblies or self-organize, possibly even forming hierarchies. The overall alignment of the local structures can be additionally improved by electric or magnetic fields, by flow, or by patterned surfaces.

To illustrate recognition-driven supramolecule formation in polymers and the subsequent self-organization and preparation of functional materials and nano-objects, we focus on the comb-shaped architecture (Fig. 1) encouraged by the enhanced solubility of so-called hairy-rod polymers. The simplest case is a flexible polymer having bonding sites along its backbone (Fig. 1A). Therefore, the backbone is typically polar, and repulsive nonpolar side groups can be connected by complementary bonds, leading to comb-shaped supramolecules, which in turn self-organize. We have extensively used hydrogen bonding or coordination to bond side chains to the polymer backbone (*18*). Antonietti *et al.* have used ionic interactions in polyelectrolyte-surfactant complexes to form comb-shaped polyelectrolyte surfactant complexes (*19*). The resulting self-organized multidomain structures may be aligned, using, for example, flow, in order to approach monodomains (*20*). One can also tune the properties by tailoring the nature of the side chains. For example, if the side chains are partly fluorinated, low surface energy results, which allows for applications that lead to reduced friction (*21*). In another case, the backbone consists of the double helix of DNA, and self-organization is achieved by ionically bonding cationic liposomes or cationic surfactants to the anionic phosphate sites (*22*, *23*). This allows for materials design beyond the traditional scope of biochemical applications. For example, dyes can be intercalated into the helices, suppressing their aggregation tendency and leading to promising properties as templates for photonic applications (*23*). In such a structure, the polymer backbone may contain two or even more kinds of binding sites where different additives can be bonded (Fig. 1B).

Side chains can also have two separate functions. For example, in addition to providing a repulsive side chain required for self-organization, the side chains may contain an acidic group that acts as a dopant for a conjugated polymer such as polyaniline, which leads to electronic conductivity (*24*). To introduce further degrees of freedom in tailoring the self-organized phases and their processing, polyaniline may first be doped by a substance such as camphor sulphonic acid and subsequently connected to hexyl resorcinol molecules using their two hydrogen bonds (Fig. 1C) (*25*). The alkyl chains of the hydrogen-bonded hexyl resorcinol molecules act as plasticizers, leading to thermoplastic processibility of the otherwise infusible polymer. They enforce self-organization where camphor sulfonic acid–doped polyaniline chains are confined in nanoscale conducting cylinders (*25*), leading to increased conductivity. The concept can be applied even to rodlike polymers, such as polypyridine, which consists of *para*-coupled heteroaromatic rings. Its optical properties can be tuned based on camphor sulphonic acid. Subsequent hydrogen bonding with alkyl resorcinol creates comb-shaped supramolecules, which self-organize in lamellae in such a way that the material is fluid even without additional solvents (*26*). Such a fluid state incorporating rigid polymeric rods is uncommon and allows processing toward monodomains where the rods are aligned. Ultimately, the plasticizing hydrogen-bonded alkyl resorcinol molecules can be removed by evaporation in a vacuum oven, thus interlocking the chains in solid stable films (Fig. 1D). In this way, efficient polarized luminance has been achieved (*26*).

To increase complexity, one can incorporate structural hierarchies. This can be accomplished by applying within a single material different self-organization and recognition mechanisms operating at different length scales. For example, block copolymeric self-organization at the 100 to 2000 Å length scale and polymer-amphiphile self-organization at the 10 to 60 Å length scale can be combined (Fig. 1E) (*18*, *27*). After selective doping of one block, conductivity can be switched based on a sequence of phase transitions (*18*). Macroscopically tridirectional protonic conductivity can be accomplished by flow-orienting the local structures (*28*). There is a rich variety of phases (*27*), such as lamellae-*within*-cylinders (Fig. 1F), which (in analogy to Fig. 1D) also allow selective cleaving of the constituents that form the supramolecules. For example, starting from polystyrene-*block*-poly(4-vinylpyridine), in which pentadecylphenol has been hydrogen-bonded, one obtains a structure in which the glassy polystyrene matrix contains empty cylindrical pores with poly(4-vinylpyridine) brushes at the walls (Fig. 1G) (*29*). By selecting different block copolymers and amphiphiles, one can tune the wettability of the pore walls. In principle, even the conformations of the brushes can be controlled by selecting the polymer and solvent properly. Saito crosslinked the poly(4-vinylpyridine) "slices," leading to a method of preparing nanoscale colloidal disks (Fig. 1H) (*30*). Other shapes of nano-objects can also be prepared as shown in Fig. 1I, which shows polymeric rods (*31*).

Structural complexity can lead to a general concept for combining different functionalities within a single material, tuning them separately, and selecting different combinations of them at different processing stages. This leads to new processing options and control of defects of rodlike conjugated polymers, which opens possibilities in molecular electronics. In addition, structural complexity also leads to properties that respond to external stimuli and conditions. Such materials may not necessarily compete with more traditional electronics or structural materials but could offer new possibilities, for example in "smart" structural parts, coatings, glues, and paints. Biological materials can also open new routes in materials science, as demonstrated by successful attempts to use the functionalities of DNA (*22*, *23*) and the strong surface activity of specific self-organizing fungal proteins (*32*). Materials science is only beginning to use all of these aspects, opening up routes to unforeseen applications.

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