Supramolecular Polymer Chemistry

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Supramolecular chemistry aims at constructing highly complex chemical systems and advanced materials by designing arrays of components held together by intermolecular forces. The implementation of molecular recognition and information offers means for controlling the evolution and the architecture of supramolecular entities and of organised phases as they spontaneously build up from their components through self-organisation.

Via recognition-directed association, self-assembly and self-organization processes, supramolecular chemistry opens new perspectives in materials science towards the design and engineering of *supramolecular materials*. The properties of a material depend both on the nature of the constituents and on the interactions between them. Supramolecular chemistry may thus be expected to have a strong impact on materials science via the explicit manipulation of the non-covalent forces that hold the constituents together. These interactions and the recognition processes that they underlie, allow the design of materials and the control of their build-up from suitable units by self-assembly. In particular polymers of supramolecular nature may be obtained by the self-assembly of monomers interconnecting through complementary recognition groups.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity. Moreover, and most significantly, the reversibility of the associations allows a continuous reorganization by both modification of the connections between the constituents and incorporation or extrusion of components by exchange with the surroundings, conferring therefore combinatorial features to the system.

Consequently, supramolecular materials are by nature *dynamic materials*, defined as materials whose constituents are linked through reversible connections and undergo spontaneous and continuous assembly/deassembly processes in a given set of conditions. Because of their intrinsic ability to exchange their constituents, they have also combinatorial character so that they may be considered as *dynamic combinatorial materials*. Supramolecular materials thus are instructed, dynamic and combinatorial; they may in principle select their constituents in response to external stimuli or environmental factors and therefore behave as *adaptive materials*.

It follows from the previous considerations that *supramolecular polymer chemistry* is both dynamic and combinatorial and that supramolecular polymers are therefore dynamic combinatorial materials based on dynamic libraries whose constituents have a combinatorial diversity determined by the number of different monomers. Similar views apply to

 CCC 1022-1360/00/$ 17.50+.50/0

supramolecular liquid crystals. The components effectively incorporated into the polyassociations depend in particular on the nature of the recognition and core groups as well as on the interactions with the environment, so that supramolecular polymers possess the possibility of adaptation by association/growth/dissociation sequences. The selection of components may occur on the basis of size commensurability, of compatibility in chemical properties, in charge, in rigidity/flexibility, etc. Depending on the nature and variety of core/interaction/functional groups in mixtures of several different monomeric components, the dynamic and combinatorial features of supramolecular polymers give access to higher levels of behavior such as healing, adaptability response to external stimulants (heat, light, additives, etc.).

Molecular information-based recognition events represent a means of performing programmed *materials engineering* and *processing* of biomimetic or abiotic type and may lead to self-assembling nanostructures, organized and functional species of nanometric dimensions that define a *supramolecular nanochemistry*, an area to which supramolecular polymer chemistry is particularly well suited and able to make important contributions.

The design of molecular information controlled, "*programmed*" and functional self-organising systems represents new horizons in supramolecular chemistry and provides a powerful approach to nanoscience and nanotechnology, in particular for the development of "smart" nanomaterials. A rich variety of architectures, properties and processes may be expected to result from the blending of supramolecular chemistry with polymer chemistry.

General References

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- For a presentation of dynamic combinatorial chemistry, see: Lehn, J.-M., *"Dynamic Combinatorial Chemistry and Virtual Combinatorial Libraries", Chem. Eur. J.*, **1999**, *5*, 2455.
- For a recent review of the present topic, see: Lehn, J.-M., *"Supramolecular Polymer Chemistry – Scope and Perspectives"*, in *Supramolecular Polymers* (A. Ciferri, ed.), Marcel Dekker, New-York, 2000, pp. 615-641.