

Supramolecular Polymer Chemistry: Past, Present, and Future

The interplay between polymer science and supramolecular chemistry leads to the formation of various supramolecular polymeric systems, with their functions determined by the range of supramolecular structures formed by self-assembly (Fig. 1). In general, there are two main approaches to fabricate supramolecular polymeric systems. In approach A, covalently linked polymers are used as building blocks to self-assemble into supramolecular polymeric systems on the basis of noncovalent interactions. In approach B, bi-functional monomers are designed and synthesized on the basis of covalent bonds, which can then self-assemble into supramolecular assemblies exploiting noncovalent interactions. Where these supramolecular assemblies exhibit macromolecular chain-like structures, they are defined as supramolecular polymers.

Covalent amphiphilic block copolymers can self-assemble into various supramolecular structures, such as crew-cut micelles, multicompartiment micelles, noncovalently connected micelles, nanospheres, hollow spheres, multilamellar vesicles, and bicontinuous double-diamond structures. The mechanism behind the self-assembly of amphiphilic block copolymers is well described in terms of thermal dynamics of microphase separation. Theoretical predictions have already led to the experimental confirmation of beautiful supramolecular structures.

In addition to the amphiphilic block copolymers formed through covalent bonds, there are polymeric supra-amphiphiles that are formed on the basis of noncovalent interactions. For example, double hydrophilic block copolymers are water-soluble, and there is no chemical basis for self-assembly. When one segment of such a double hydrophilic block copolymer interacts with hydrophobic building blocks on the basis of electrostatic interactions, it forms polymeric supra-amphiphiles, with the newly induced amphiphilicity responsible for self-assembly.

As mentioned before, supramolecular polymers formed on the basis of noncovalent interactions can exhibit macromolecular chain-like properties, such as viscoelasticity. To this end, supramolecular polymers with high molecular weight need to be fabricated, with the degree of supramolecular polymerization dependent on the strength of noncovalent interactions. Considering that interactions between metal ions and ligands are strong enough, such metal ion-ligand coordination bonds can be used to drive supramolecular polymerization directly. There are several ways to enhance other weak noncovalent interactions. For example, monotopic hydrogen bonding is too weak, while quadruple hydrogen bonding is strong enough to drive supramolecular polymerization. In addition, here a further example to enhance the strength of weak noncovalent in-

teractions: weak charge-transfer interactions between the two guests can be amplified significantly when the two guests are incorporated into the cavity of a supramolecular host, *e.g.*, cucurbit[8]uril. It has been demonstrated that supramolecular polymers with high molecular weights can be formed on the basis of host-enhanced charge-transfer interactions. Interestingly, similar strategies can be extended to enhance π - π interactions, polar- π interactions, and others, which can drive supramolecular polymerization as well.

The mechanism of supramolecular polymerization is usually divided into three major types, namely, isodesmic, ring-chain, and cooperative supramolecular polymerization. A variety of effective methods for supramolecular polymerization, from controllable fabrication to living polymerization, have been established and developed based on the growth mechanisms. These methods mainly include seeded supramolecular polymerization, chain-growth supramolecular polymerization, supramolecular polymerization promoted through self-sorting, covalent polymerization of supramonomers, supramolecular interfacial polymerization, and dissipative supramolecular polymerization. By means of the methods above, the synthesis of supramolecular polymers with controlled chain structure and molecular-weight distribution can be achieved through thermodynamic and kinetic pathway control.

In addition to the conceptual and structural beauty that supramolecular polymeric systems have brought to us, we should consider if there is functional beauty behind self-assembly. It is well known that the self-assembly of block copolymers can provide a nanotechnology for surface patterning, so-called block copolymer lithography. However, it is not easy to fabricate defect-free surface patterns of pre-determined size. Block copolymer micelles can work as reaction templates, and nanomaterials can be synthesized in the confined space of such micelles. Drug delivery has been explored extensively for biocompatible block copolymers. Recently, it has also been demonstrated that polymer vesicles can be used as microenvironments for a green synthesis of polymers with tailor-made stereo-structures.

The dynamic nature of noncovalent interactions can endow supramolecular polymers with unique properties, for instance, reversibility, adaptiveness, self-healing, and stimuli-responsiveness. Therefore, supramolecular polymeric materials show a variety of applications in multi-disciplinary fields, including degradable and recyclable materials, self-healing electronic devices, stimuli-responsive drug carriers, and shape-shifting materials. It should be pointed out that research into supramolecular polymeric systems is not limited to fundamental research, and is already com-

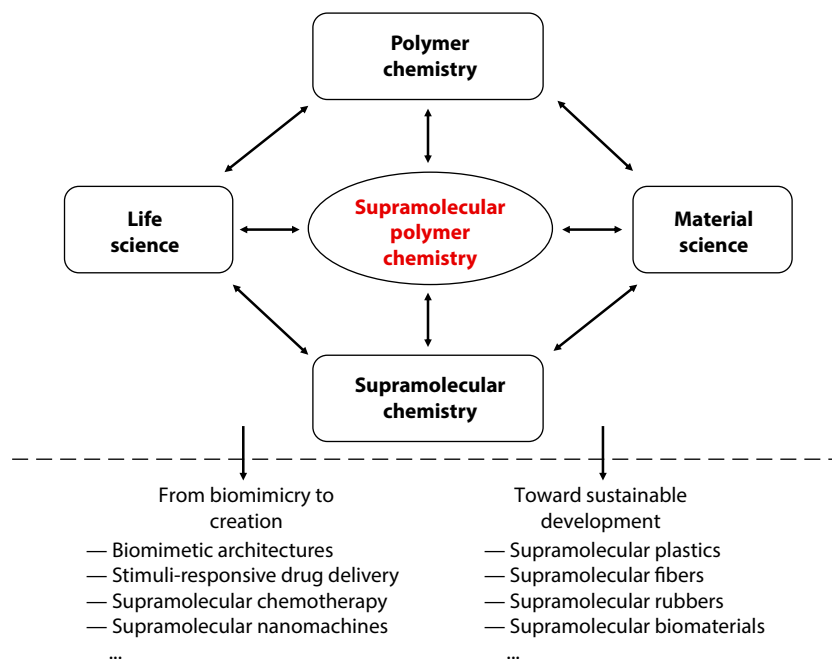


Fig. 1 Supramolecular polymer chemistry as an interdisciplinary field of science.

mercially available as self-healing materials (by Suprapolix) and degradable biomaterials.

When was the field of supramolecular polymer chemistry launched? You may have different answers depending on whom you ask. It could date back to the 1960s, when research into liquid-crystalline polymers began. The self-assembly of amphiphilic polymers at interfaces could be considered as the origin of supramolecular polymer chemistry. Moreover, helical polymers belong to the realm of supramolecular polymer chemistry as well. Therefore, there are many well-known scientists in Europe, North American, Japan, and China who have made significant contributions to shaping and extending the field of supramolecular polymer chemistry.

Although we all have witnessed that supramolecular polymer chemistry is bridging the gap between materials science and life science, it is still in an early stage of development, and more questions are raised than answered. The hope is that many new ideas will arise from the inspiration provided by biological organisms. One can mimic the delicate supramolecular structures and functions of biological organisms. More importantly, one needs to go one step further from biomimicry to creation, to create supramolecular polymeric systems with robust structures and improved functions. In doing so, the combination of the advantages of covalent bonds and noncovalent interactions is a good choice, with covalent bonds for robust-

ness and noncovalent interactions for reversible and dynamic properties. Therefore, a new set of supramolecular polymeric materials with balanced stability and dynamics that could be recycled and regenerated, such as supramolecular plastics, supramolecular fibers, and supramolecular rubbers, may be developed. In other words, supramolecular polymer chemistry can provide the scientific basis for solving some of the problems relevant to global sustainable development.



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The views expressed in this editorial are those of the author.