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# Supramolecular interactions for controlling the structure, self-organization and dynamics of stimuli-responsive polymeric systems

## Abstract

*This research is aimed at the development of novel nanostructured functional materials with intrinsic self-healing and “smart” properties. With the concern of approaching practical applications, an unprecedented control was achieved over the molecular structure, organization and dynamics of a versatile class of soft material. Inspired by the biological processes and assemblies occurring in Nature, the creation of those structurally-defined materials was possible by the hierarchical organization of synthetic building blocks over multiple levels of assembly. Starting at the molecular scale with the chemical synthesis of a library of tailored molecular building bricks, this research has extended to their bio-inspired assembly at the nanoscale and toward gel-like materials with precisely controlled architectures. Given the truly enormous variety of molecular building bricks and resulting architectures achieved through this strategy, the physics of the engineered materials was varied by orders of magnitude, ranging from low viscous solutions to highly elastic solids. In addition, the hierarchical structure of the materials led to a parallel hierarchy of dynamic processes, capable of adjustments in response to a wide variety of physical and chemical constraints.*

## Keywords

*supramolecular polymers, self-healing materials, rheology*

## 1. Introduction

Since polymeric materials constitute the technological driving force of the 20<sup>th</sup> century, the quest for implementing self-healing properties into polymers is sustained. However, most modern materials are indeed still subject to mechanical destruction as well as chemical degradation, restricting their use. Since the early 2000's, three conceptual approaches have been thus developed toward self-healing polymeric materials, each having advantages and limitations (Figure 1) [1]. Among them, intrinsic self-healing systems exploit the reversible nature of physical bonds to incorporate healing abilities directly into the material.

In parallel to the quest for self-healing, “smart” materials, *i.e.*, whose properties can be significantly changed in a controlled fashion by external triggers, are experiencing an unprecedented development over the last few years. “Smart” materials have been designed to support a range of properties pertaining to be used in various environments. At the basis of those materials lie intelligent (macro-)molecules having the capability to adapt their conformational structures and/or properties in response to external stimuli such as stress, temperature, moisture, pH, redox, electric or magnetic fields [2,3]...

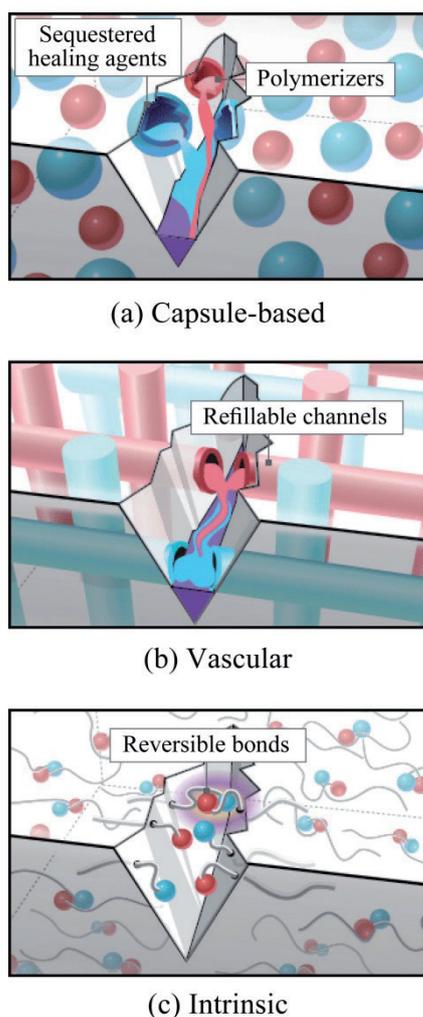


Figure 1: Different approaches to self-healing polymers [1]

## 2. Design strategy

In the last years, the advent of supramolecular chemistry has provided chemists with new possibilities to synthesize complex structures and dynamic materials by self-assembly. In particular, the creation of structurally defined materials is possible by applying the concept of hierarchical

self-assembly, *i.e.*, the spontaneous non-covalent organization of molecules and macromolecules over distinct multiple levels (Figure 2), in which the assembly processes gradually decrease in strength [4,5]. In turn, the hierarchical structure of the assemblies leads to a parallel hierarchy of dynamic processes, capable of adjustments in response to a wide variety of stimuli including temperature, chemical environment, and mechanical stress.

By virtue of their properties, metal–ligand interactions are particularly promising for the synthesis of supramolecular polymers and the construction of “smart” materials with self-restructuring abilities. Indeed, those interactions are relatively strong and give access to a wide library of organic ligands, along with appropriated metal ions including nearly half the periodic table [6]. In supramolecular architectures, metal–ligand association can be further combined with many other non-covalent binding interactions, in an orthogonal way [7,8]. In addition, significant changes in the structure, kinetic and thermodynamic stability of the resulting assemblies can be readily achieved depending on the metal–ligand pair [9,10].

In order to build reliable supramolecular polymer materials, macromolecular building blocks are essentials, especially those with well-defined and chemically tailored architecture. To circumvent the major drawback and limitations of classical synthetic strategies, a versatile approach was conceptually developed based on the self-assembly behavior of block copolymers into star-like micelles bearing coordination motifs in their corona (Figure 3). Following this idea, the size, stability and functionality of these nanostructured motifs was controlled according to the length of the different polymer sequences constituting the so-called block copolymers. The accordingly obtained micelles

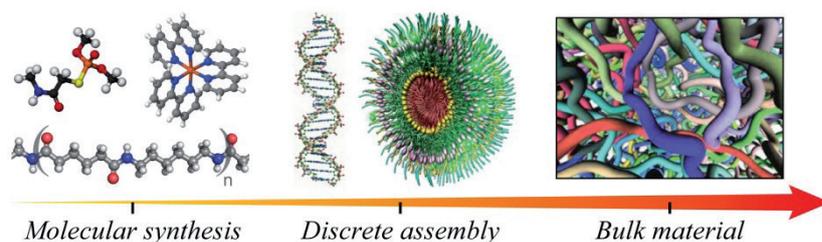


Figure 2: Hierarchical self-assembly across scales

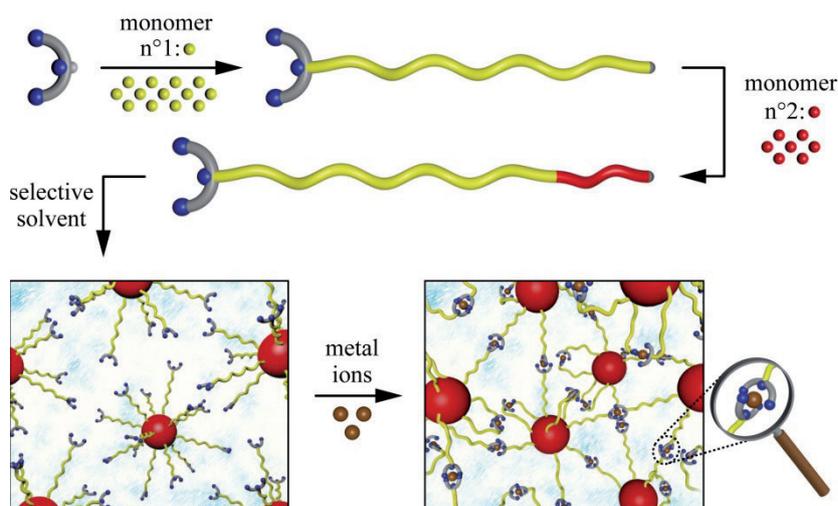


Figure 3: Chemical synthesis and hierarchical assembly of ligand end-functionalized block copolymers into coordination micellar gels

represented the first level of self-assembly in the context of the hierarchically-organized materials. The second level of organization was attained in presence of metal ions by creating reversible associations between micellar objects toward the formation of a three-dimensional rubber-like network (Figure 3).

### 2.1. Synthesis of building bricks

To introduce a coordination motif in the architecture of macromolecular chains, two main strategies can be envisaged that consist in either the post-modification of pre-synthesized polymers, or the use of functional reactants during the polymerization process [11]. If both approaches present advantages and drawbacks, the second is more versatile in nature, offering better control over the number and position of incorporated functional groups. Following this strategy, a synthetic route was developed toward block copolymers having a functional terminus that involved sequential controlled polymerization techniques of various monomeric units (Figure 3) [12,13]. From the main categories of styrene, (meth-)acrylate, and acrylamide monomers, three well-studied candidates were selected to afford various macromolecular building bricks shown in Figure 4, each having specific characteristics: polystyrene (PS), poly(*N*-isopropylacrylamide) (PNIPAAm), and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA). In this respect, stimuli-sensitive polymer sequences were used as core-forming blocks to control the self-assembly into micelles, or employed as corona-forming blocks to modulate the conformation of chains bridging micellar cores.

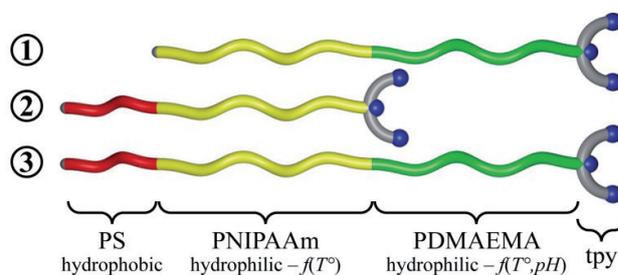


Figure 4: Various macromolecular building blocks having ligand terminus

### 2.2. Assembly of building bricks

The synthesized macromolecular building bricks were assembled over distinct levels of hierarchy to yield supramolecular materials, as schematized in Figure 3. In practice, the assembly behavior of the different copolymers was monitored in solution by a combination of analytical techniques such as light scattering, microscopy imaging, chromatographic and spectroscopic methods [12,13]. At first, micellization was achieved by dissolution of the block copolymers in a selective solvent for the corona-forming blocks, or specifically triggered by other stimuli. Decorated with coordination motifs at the end of each coronal chain, the micellar nano-objects constituted formidable precursors for cross-linked materials. Thanks to the coordination of two ligands around a metal center, adding metal cations to these systems triggered the formation of active metallo-bridges between micellar nanostructures, which resulted in the formation of three-dimensional network and thus gelation (Figure 5) [14].

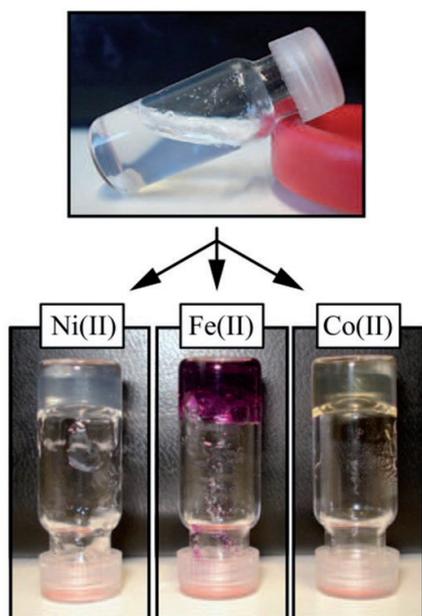
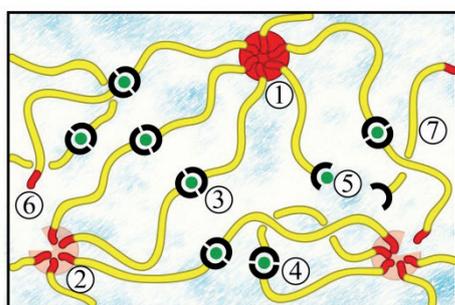


Figure 5: Pictures of supramolecular hydrogels obtained from a micellar solution upon the addition of different transition metal ions [14]

### 3. Rheological characterization

At the core of this research, the dynamic mechanical properties of the assembled rubber-like materials were deeply investigated using rotational rheometry measurements in order to establish relationships between their structures, dynamics and mechanical properties [14-16]. Due to their highly complex structure and organization, they were indeed suited to serve as ideal systems for studying their dynamics, which in turn allow self-healing events. Not surprisingly, the structural complexity and hierarchical organization of the studied materials



- ① frozen micellar core    ② transient micellar core  
 ③ inter-micellar bridge    ④ intra-micellar loop  
 ⑤ pendant coordination    ⑥ pendant hydrophobe  
 ⑦ free polymer chain

Figure 6: Richness of network configurations in coordination micellar gels

was accompanied by a relatively rich flow behavior. Indeed, the engineered material adopted numerous configurations that were precisely controlled depending on the characteristics of the associating building blocks and the conditions for their self-assembly (Figure 6).

At first, the linear viscoelastic response, *i.e.*, dynamics and cross-linking density, of the jelly materials were closely related to the structural characteristics of the transient networks. Interestingly, their dynamic behavior reflected the discrete contributions from each transient cross-linker, being respectively tuned by the length of the aggregating segment and the nature of metal ions. Depending on the stability of both micellar and metal–ligand associations, the viscoelastic response of the self-assembled materials was varied from that of highly elastic gels to the one of more viscous solutions, each having their own rheological signature [14]. In parallel, the cross-linking density and strength of the hierarchically assembled materials was adjusted by controlling the fraction of elastically active inter-micellar bridges in the system, compared to inactive intra-micellar loops. To achieve that goal, several factors were successfully investigated that are the length, volume fraction, swelling, and degree of functionality of the associating copolymer (Figure 7) [15].

The surrounding environment of the network constituting a perfect transmission media, the ability of the developed materials to respond to environmental changes, *e.g.*, pH or temperature, was

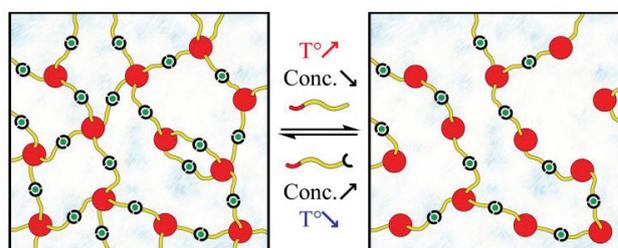


Figure 7: Tuning the cross-link density of coordination micellar gels

monitored and rationalized by the solution behavior of the associating copolymers. By chemically targeting the transient associations structuring the networks, an orthogonal control was gained over the dynamics of the materials, which is essential for stress relaxation and healing. Among stimuli, a particular attention was paid to mechanical stress, with the possibility to achieve reversible breaking, and thus healing, of the associating junctions of the transient networks [14]. In addition, using stimuli-sensitive coronal block allowed controlling the swelling of the supramolecular gel by changing the pH or temperature of the surrounding media. Finally, stimuli-responsive properties were also imparted to the core-forming block(s), leading to the assembly, disassembly or strengthening of micellar cores upon application of the stimulus (Figure 8) [16].



Figure 8: Pictures showing the thermo-induced assembly and disassembly of a coordination micellar gel

#### 4. Conclusion

In this study, the use of metal–ligand interaction in combination with classical macromolecular architectures has proved to be a straightforward approach towards supramolecular multi-responsive polymeric materials with control over their structure, organization and dynamics. From an applied point of view, this study has provided a

design strategy and guidelines for the elaboration of supramolecular polymeric materials with controlled properties. From a more fundamental point of view, this work has established clear relationships between the structure and rheological properties of a particular class of self-assembled materials. Finally, this research offers exciting breakthroughs to drive future developments and possible applications in the field of material sciences and engineering.

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