

# Self-healing Supramolecular Metallopolymers

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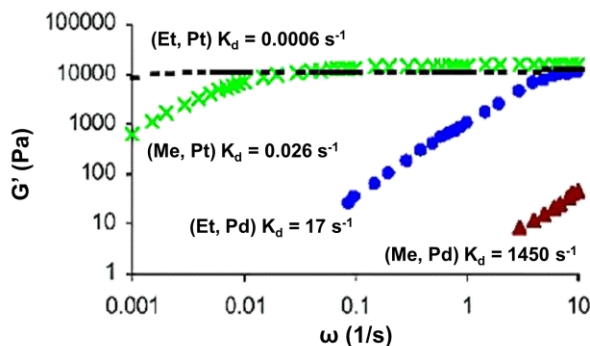
Literature Seminar

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Used to engineer surface coatings, children's toys, and car parts, polymers have become an integral part of our lives over the past one hundred years. Their light weight, processability, and stability in atmospheric conditions make polymers ideal for a variety of engineering applications;<sup>1</sup> however, their long-term strength and durability are compromised by their tendency toward micro-cracking, a phenomenon that often leads to catastrophic failure. Since autonomous self-healing was first proposed as a potential solution to this problem in the 1980's,<sup>2</sup> research on self-healing polymeric materials has grown rapidly. In conventional polymers, the high molecular weight hydrocarbon backbone consists of irreversible covalent interactions, which break during crack formation. If the polymer is a thermoplastic, "self-healing" is possible by heating the polymer above the glass transition temperature, enabling polymer chains to flow together and re-entangle. Although this does regain most of the polymer strength, the process is slow ( $\propto MW^3$ ) and the location where "healing" occurs is subject to fatigue.<sup>1,2</sup>

Modern advancements in self-healing materials can be divided into two categories: materials that heal through the formation of new bonds (e.g., via microcapsules that release uncured polymeric material when fractured) and those that heal through the re-assembly of bonds already present (e.g., Diel's Alder, H-bonding, and coordination complexes).<sup>1,3</sup> An advantage of the latter mechanism is the ability to repeatedly self-heal in the same location without having to replenish the healing materials. Introducing reversible interactions into the polymer backbone through metal-ligand coordination complexes yields a dynamic structure in which there is a continuous change in bound and free monomers, molecular weight, and degree of polymerization. Also, the incorporation of metal ions offers the potential for alternative healing stimuli (e.g., redox, magnetic, or optical). Additionally, since metal-ligand bonds can break and recombine easily, small external stimuli, like heat, light, or mechanical stress, can lead to rapid and significant changes in viscosity. Researchers are exploiting this phenomenon to increase healing efficiency and decrease healing time.<sup>4</sup>

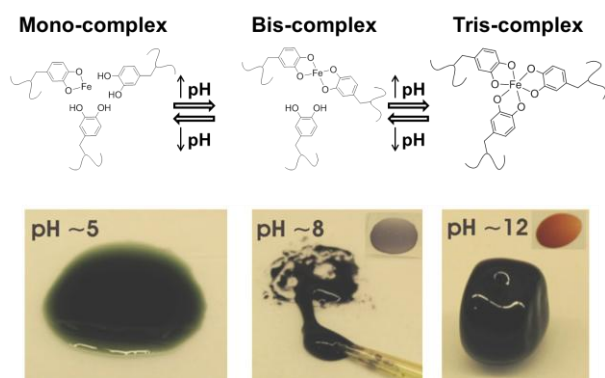
Much of the current literature on self-healing supramolecular metallopolymers (SMPs) falls into one of three approaches. The first approach, studied extensively by Stephen Craig at Duke University, is the use of pincer complexes as polymeric cross-linkers. These complexes incorporate two Pd(II) or Pt(II) metal centers that each have the potential to bind to a polymer side-chain pyridine ligand.<sup>5,6</sup> Perhaps their most interesting studies demonstrate the influence of metal-ligand bonding kinetics on a polymer gel's dynamic mechanical properties. Figure 1 shows the dependence of the metal-ligand bond



**Figure 1:** Oscillatory rheology data depicting the storage elastic modulus ( $G'$ ) for different pincer complexes. A slower dissociation constant leads to a stronger material under the same strain rate.

on the storage elastic modulus ( $G'$ ) of organogels as measured by oscillatory rheology.<sup>5</sup> Additionally, changing the side-chains of the pincer complex from methyl to ethyl and changing the metal from Pd(II) to Pt(II) increased the polymer's viscosity.<sup>5</sup> Although Craig and co-workers have yet to publish a self-healing system using this technology, their work has demonstrated the dynamic and stress-bearing nature of these pincer cross-linked systems.

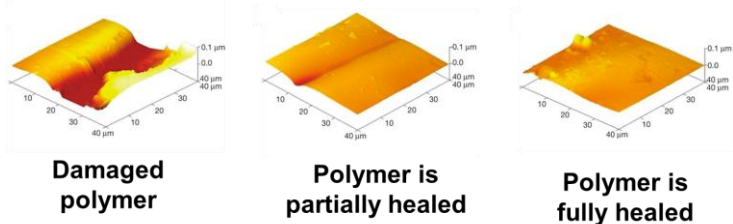
Because the bonds in these self-healing SMPs are dynamic and reversible, a reoccurring problem in the field of self-healing SMPs is low material strength. It was recently demonstrated that dynamic  $\text{Fe}^{3+}$ -catechol complexes suppress micro-crack formation in mussel byssal threads,<sup>7</sup> and also that mussel byssal threads have high strength and extensibility.<sup>8</sup> In light of these findings, there has been an influx of research on self-healing SMPs that mimic these threads.<sup>8-9</sup> Recently, Holten-Anderson et al. formed a  $\text{Fe}^{3+}$ -catechol cross-linked polymer gel that showed pH-dependent viscosities (Figure 2). The polymer demonstrated self-healing properties, regaining full strength after 3 minutes, and was claimed to possess a “near-covalent”  $G'$  value. The  $G'$  of the covalent gel (PEG-dopa<sub>4</sub>) and the  $\text{Fe}^{3+}$  cross-linked gel were similar in magnitude, about 1 kPa, only at high strain rates.<sup>9</sup> It is interesting to note that this value is even lower than that of the gel reported by Craig and co-workers.



**Figure 2:** pH-dependence of  $\text{Fe}^{3+}$ -catechol complex formation and how the differences manifest in the macroscopic polymeric gel.

Some researchers have looked to self-healing SMPs initiated via external stimuli to increase material strength.<sup>10-12</sup> Burnworth et al. recently reported an SMP that could self-heal upon exposure to light in just one minute. This is dramatically faster than most other self-healing mechanisms ( $\sim 10$  min to  $> 24$  hrs).<sup>1,3</sup> The polymer structure is comprised of a poly(ethylene-*co*-butylene) backbone and is cross-linked via metal-mebip coordination complexes. The self-healing mechanism relies on absorption of UV light by the metal-mebip complexes and the conversion of this energy to heat. The energy breaks the metal-mebip cross-links, and a corresponding dramatic decrease in viscosity is observed. This allows the crack to rapidly fill with polymer, and as the polymer cools, the reversible metal-mebip bonds reform (Figure 3). Similar to others in this field, Burnworth et al. found that metal-ligand complex lability produces opposing effects on material

**Figure 3:** AFM images of  $\text{La}^{3+}$  SMP. Two 30-second exposures to UV irradiation are sufficient for full healing.



strength and healing efficiency.<sup>13</sup> The Zn<sup>2+</sup> polymer had a higher tensile strength than the more labile La<sup>3+</sup> polymer; however, this higher tensile strength corresponded to a lower healing efficiency.<sup>12</sup>

The field of supramolecular metallopolymers holds promise in the application of self-healing materials. The reversible nature of the metal-ligand bond, the increased strength with respect to other supramolecular interactions (e.g., hydrogen bonding), and the response of metal complexes to external stimuli all suggest that SMPs have the potential to be both strong and long-lasting materials.

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