

# METALLOPOLYMERS AS SELF-HEALING MATERIALS

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## ABSTRACT

Metallopolymers represent an interesting class of supramolecular polymers. Their properties can be tuned by the selection of the attached/incorporated ligand as well as the choice of the corresponding metal ion.[1] In this manner, also reversible interactions, *i.e.* on the one side undirected ionic interactions between positively charged metal complexes and negatively charged counterions as well as on the other side directed ligand-metal interactions can be introduced. These interactions are the basis for the introduction of self-healing properties, comparable to the natural archetype (reversible metal complexes can be found within mussel byssus threads).[2] Different methacrylate-based polymers containing ligands (*i.e.* terpyridine) in the sidechain have been synthesized. These materials have been used for the fabrication of cross-linked metallopolymer networks. The influence of the comonomers, the binding ligand as well as the metal ion on the resulting cross-linked polymer films has been investigated in detail. Additionally the influence of the counter ion on the polymeric films has been studied. The self-healing behavior of these materials was investigated. Lastly, the basic mechanisms behind the self-healing processes within these metallopolymers will be discussed in detail.

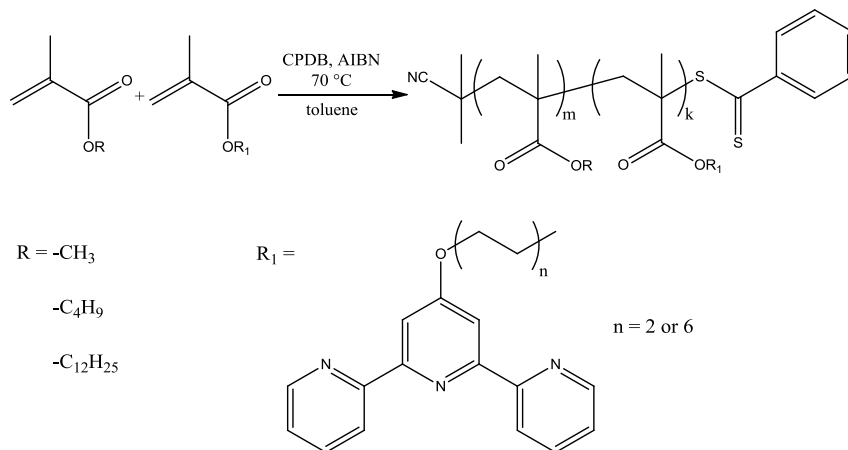
## 1. INTRODUCTION

Metallopolymers combine typical properties of metals (*e.g.*, conductivity) as well as polymeric properties (*e.g.*, film formation). The resulting properties can be tuned by the choice of the ligands as well as the corresponding metal ions; the nature of the resulting metal complexes influences the polymer properties. The binding strength of the metal complexes can be adjusted: complexes with binding strengths comparable to covalent bonds as well as dynamic and weak complexes can be obtained.

In the context of self-healing materials weaker and more dynamic complexes are preferable. Therefore the required mobility for the self-healing process can be induced easier, *e.g.*, by a decomplexation/rearrangement of the metal complexes.[3] Different copolymers containing terpyridine as binding ligand were synthesized and subsequently crosslinked by different metal ions.[4] The properties of the resulting crosslinked polymer networks have been investigated.

## 2. MATERIALS AND METHODS

A library of different copolymers (terpyridine containing polymers as well as alkylmethacrylates comonomers) was synthesized using the reversible addition/fragmentation chain transfer (RAFT) polymerization (Scheme 1).



Scheme 1: Schematic representation of the synthesis of the polymer library.

The resulting polymers were characterized by <sup>1</sup>H NMR spectroscopy (composition, ratio of both functional groups), SEC (molar mass as well as molar mass distribution), MALDI-TOF MS (molar mass), TGA and DSC measurements (thermal properties). Moreover the polymers were crosslinked with different metal ions (e.g., iron(II), cadmium (II)). The mechanical properties as well as the self-healing behavior of the polymers were investigated.

## 3. RESULTS

The synthesized polymers (methyl methacrylate, butyl methacrylate, lauryl methacrylate) feature – as expected – different glass transition temperatures. Therefore the resulting copolymer networks will feature different mobility, which will influence their healing behavior. Subsequently, the linear, soluble polymers were crosslinked by the addition of different metal ions (Fe(II), Cd(II)). Additionally, the counterions have been varied in case of the cadmium(II).

The self-healing of the hard crosslinked films was investigated by an optical microscope. The healing of an iron(II) crosslinked polymer is depicted in Figure 1. A temperature of 100 °C was required for the healing process (if lauryl methacrylate was used as a comonomer). This temperature could only be reduced in the case of cadmium acetate as crosslinking metal salt. The resulting networks could be healed at 80 °C.

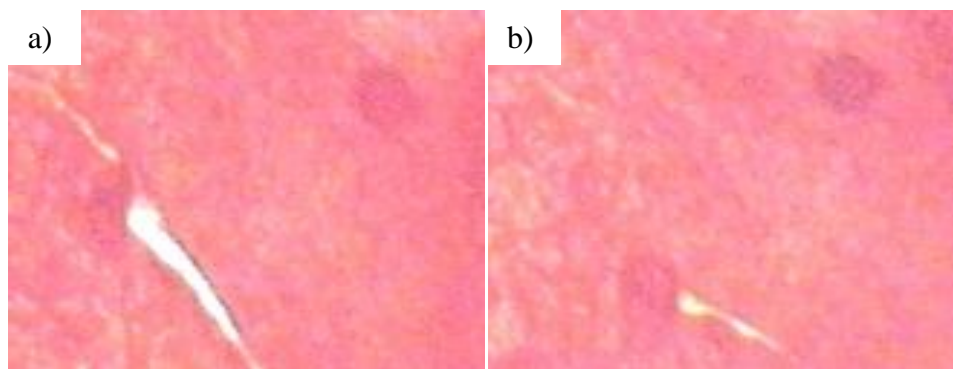


Figure 1: Self-healing of a scratched film (based on iron(II)) a) Scratch and b) healing after 16 h at 100 °C.

The healing of these metallopolymer networks is presumably based on two contributions, which depend on the nature of the metal ion (Figure 2). If weak and dynamic metal complexes are applied, decomplexation and rearrangement of the complexes can induce the required mobility. Additionally, the ionic metal complexes can induce a formation of ionic clusters. The rearrangement of these clusters can also induce the required mobility (also without the opening of the complexes).

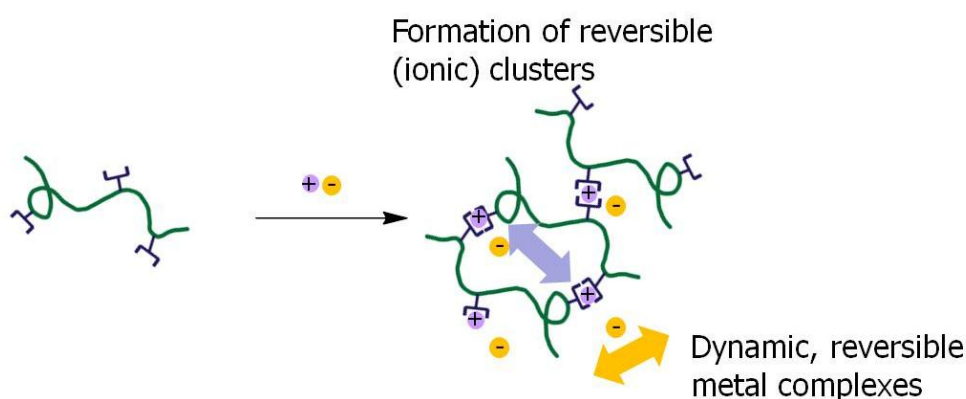


Figure 2: Schematic representation of the self-healing metallopolymer networks.

The healing of the iron(II)-based polymer networks is presumably based on the presence of the described ionic clusters. In contrast, polymer networks based on cadmium(II) acetate feature also dynamic metal complexes due to the acetate counterion, which can lead to bridged metal complexes.

#### 4. CONCLUSIONS

Metallopolymers are interesting candidates for self-healing polymers. The combination of the right ligands with the corresponding counterions can lead to an efficient self-healing of these systems. Both, the cation as well as the anion, have a great influence on the self-healing. The further elucidation of the healing mechanisms within metallopolymers can be used for the design of better self-healing polymers.

## ACKNOWLEDGEMENTS

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