SELF-HEALING METALLOPOLYMERS: DETAILED INVESTIGATION OF THE SELF-HEALING PROPERTIES BY SCRATCH TESTING

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ABSTRACT

In the last decade several intrinsic self-healing materials have been developed in which the healing mechanism was mainly based on the reversibility of a certain structural element. For this purpose, reversible covalent bonds, *e.g.*, based on the Diels-Alder reaction or weaker non-covalent interactions, *e.g*., hydrogen bonding, ionic interactions or π-π interactions, have been successfully utilized. In contrast, only few examples describe the self-healing of polymeric materials based on reversible metal-ligand-interactions, although this concept can be observed in nature (*e.g.*, in mussel byssus threads). The directed interaction between a metal ion and corresponding ligands offers the possibility to integrate a reversible unit into a polymer matrix. If metal complexes are used as structural units to promote self-healing, a compromise between the mechanical properties and the self-healing behavior must be found. Typically, the strength of the metal-ligand bond is the key factor for both. However, weaker metal complexes would promote the healing while, at the same time, the mechanical stability is reduced. The analysis of the self-healing capacity and the mechanical properties are central in order to design new functional materials.

The terpyridine ligand was chosen as a model system to study the parameters for the resulting polymer properties. For this purpose, terpyridine containing polymers were synthesized and subsequently crosslinked with different metal salts, which offers the possibility to understand the influence of the crosslinking unit, the cation and the counterion. The resulting polymeric materials were investigated in detail (*e.g.*, by scratch testing) to obtain a better insight into the self-healing behavior of the material.

1. INTRODUCTION

Self-healing materials can be defined as materials which are able to heal local mechanical damage, such as cracks or scratches. The (partial) recovery of the drop in mechanical properties as a result of local damaged sites without major external manipulation represents an intriguing feature of such materials. If the mechanism of healing is not related to an added external component, but is linked to the molecular architecture of the polymer itself, the resulting intrinsic self-healing behavior enables the ability to design novel materials, which can theoretically heal themselves endlessly, if the right healing mechanism is applied.[1,2]

In principle, metal-ligand interactions can also be used for intrinsic self-healing, as the reformation of coordinative bonds does not require demanding conditions such as high pressure or the addition of further substances, but it can occur *in-situ* for polymers in a suitable environment.[3]

The terpyridine moiety, which was used frequently, represents a well investigated polypyridyl-type ligand and the corresponding properties, *e.g.*, the complex stabilities are well-known in literature.[4] However, the reported values always refer to the solution state and the solid-state behavior of terpyridine metal complexes is still rather unexplored.

Thus, we investigated polymers, which were functionalized by terpyridine moieties and afterwards crosslinked by metal salts. We want to understand the healing mechanism behind and to combine mechanical stability and self-healing properties in metallopolymer coatings.

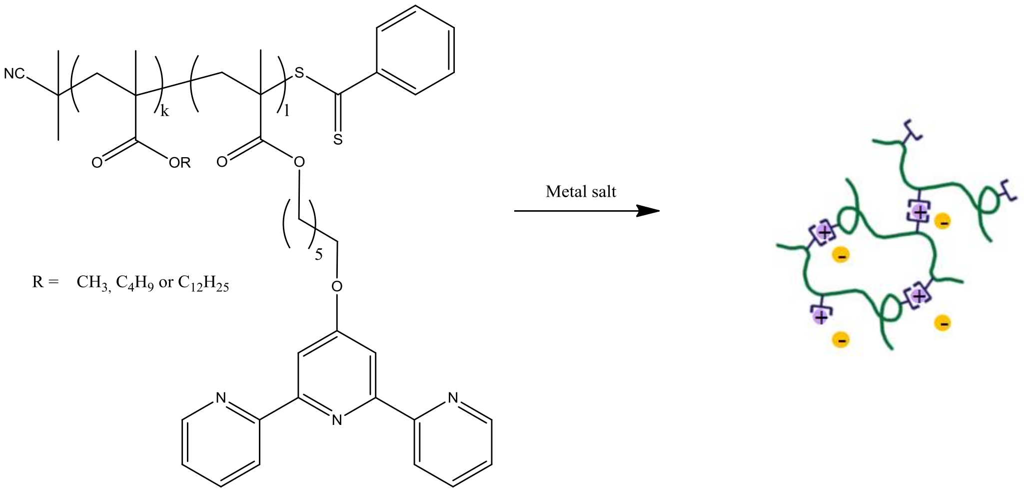
2. RESULTS AND DISCUSSION

Firstly, it is necessary to design the terpyridine containing copolymers. For this purpose, a terpyridine monomer was copolymerized with other monomers (i.e. alkyl methacrylates), in order to adjust the amount of the crosslinking units as well as to tune the thermal and mechanical properties of the resulting polymer networks. The RAFT-polymerization technique was used to obtain well-defined polymers with adjustable composition.[5] For the copolymerization three different methacrylate monomers were used: methyl methacrylate, butyl methacrylate and lauryl methacrylate. The resulting polymers have molar masses (M_n) of about 30,000 g/mol and differ in the glass transition temperature, which indicates the different flexibility/mobility of the polymer backbones. The desired content of terpyridine of 10% could be nearly reached for all polymers. Afterwards the terpyridine containing copolymers were crosslinked by the addition of a metal salt, *i.e.*, iron(II) and cadmium(II) salts (Scheme 1).

To identify the influence of the counterion on the self-healing process different cadmium(II) salts (*i.e.*, the chloride, bromide, iodide, and acetate) were used; these anions differ both in size (from 162 pm to 220 pm) and polarizability.

It could be shown that the polymer networks crosslinked with cadmium acetate shows the best self-healing behavior. The results could be explained by a phase transition, which could be detected by DSC, SWAXS and TMA-measurements. The SWAXS results are depicted in Figure 1.

The self-healing behavior was initially observed by optical microscopy. The healing process of the cadmium acetate crosslinked metallopolymer takes place at temperatures above 70 °C as shown in Figure 2.



Scheme 1: Schematic representation of the synthesis of metallopolymer network.

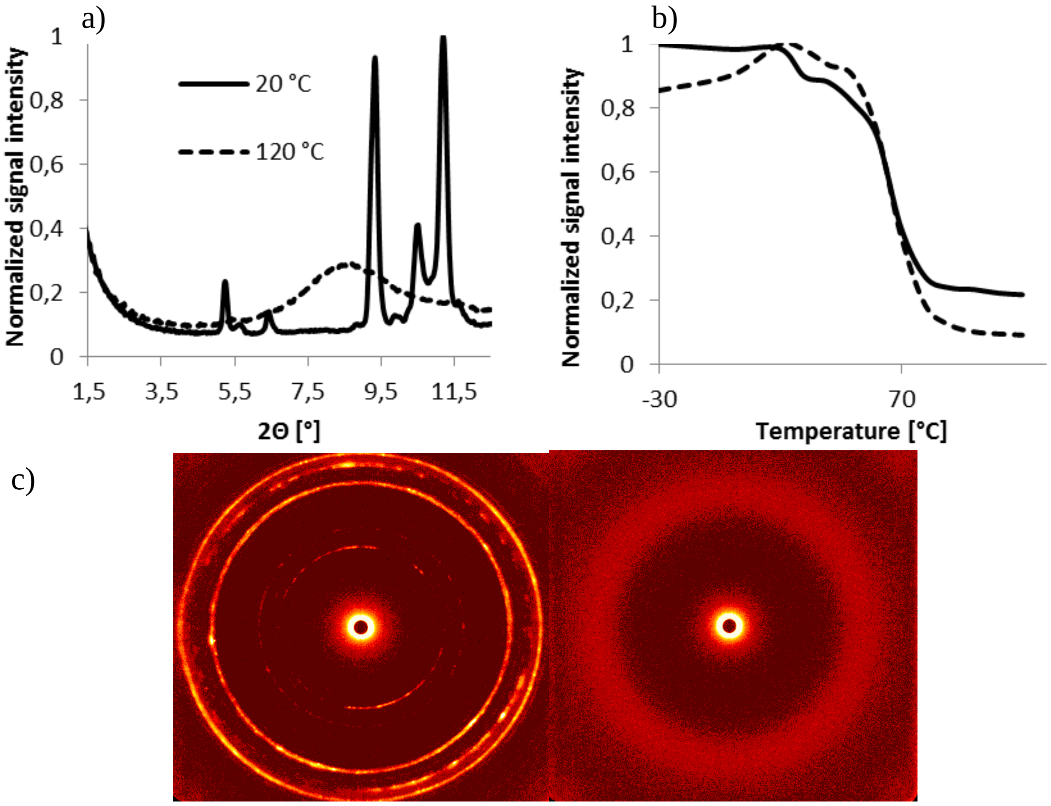


Figure 1: SWAXS results of the cadmium acetate crosslinked metallopolymer: a) SWAXS diagram at 20 °C (solid black line) and at 120 °C (dotted black line), b) signal intensity of the signal at 9.34° (solid black line) and 11.18° (dotted black line) as a function of the temperature, c) SWAXS signal at the 2D-detector at 20 °C (left) 120°C (right).

It could be noted that the copolymers were also crosslinked by the addition of other metal salts (iron (II) sulfate, cadmium (II) chloride, bromide and iodide), although these new polymers didn't lead to a significant improvement of the healing capabilities.[6] The results show a strong dependency of the healing efficiency on the cation and anions used during the crosslinking step.

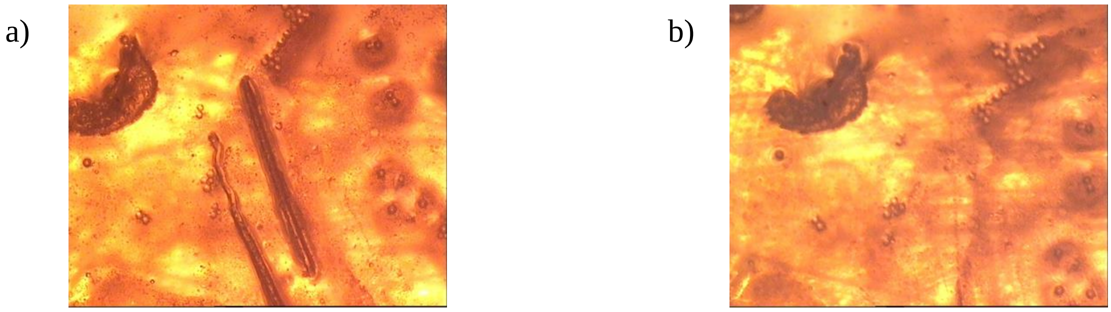


Figure 2: Self-healing experiments of the cadmium acetate crosslinked metallopolymer: a) Scratch and b) Healing after 16 h at 80 °C.

3. CONCLUSIONS

In this study, it could be shown, that metallopolymer networks are able to heal mechanical damage. The influence of the counterion was studied and it could be shown, that a copolymer, which was crosslinked by the addition of cadmium acetate shows the best self-healing behavior. This is based on the transition of the polymer and above 70 °C the acetate moieties exchange. This results in very good self-healing. Further research is being performed to gain a major understanding of the role of the different cations on the healing capabilities.

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REFERENCES

[1] M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag, U. S. Schubert, Self-healing materials, Advanced Materials 22 (2010), 5424-5430.
[2] U. Lafont, H. van Zeijl, S. van der Zwaag, Influence of Cross-linkers on the Cohesive and Adhesive Self-healing Ability of Polysulfide-Based Thermosets, Applied Materials and interfaces 4 (2012) 6280-6288.
[3] G. R. Whittell, M. D. Hager, U. S. Schubert, I. Manners, Functional soft materials from metallopolymers and metallosupramolecular polymers Nature Materials 10 (2011) 176-188.
[4] A. Wild, A. Winter, F. Schlütter, U. S. Schubert, Advances in the field of π-conjugated 2,2':6',2''-terpyridines Chemical Society Reviews 40 (2011) 1459-1511.
[5] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer : The RAFT Process Macromolecules 31 (1998) 5559-5562.
[6] S. Bode, L. Zedler, F. H. Schacher, B. Dietzek, M. Schmitt, J. Popp, M. D. Hager, U. S. Schubert, Self-healing polymer coatings based on crosslinked metallosupramolecular copolymers Advanced Materials DOI: 10.1002/adma.201203865.