MECHANICALLY ACTIVATED OLEFIN COMPLEXES OF COINAGE METALS AS CATALYSTS FOR THE RING-OPENING POLYMERIZATION OF EPOXIDES IN THE AUTONOMOUS SELF-HEALING OF COMPOSITE MATERIALS

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Keywords: Self-healing, Ring-Opening Polymerisation, Mechanophore, Catalyst

ABSTRACT

Mechanically-activated ("mechanophore") catalysts are a recent innovation, in which a latent catalyst is activated by mechanical removal of auxiliary ligand(s). [1] To date, this has been achieved by incorporating long chain substituent (for example, polyTHF) on the ligand; [2] such functionalisation is required to transfer macroscopic mechanical forces to the small metal complex; shear forces (often via sonication) induce bond scission in polymers but not in small molecules. An alternative approach is to incorporate metal and ligands as part of a coordination polymer framework. [3] This mechanophore methodology clearly offers a great deal of promise in autonomous self-healing applications, where the damage event itself could act as the trigger for catalyst activation. This contribution will describe a new family of mechanically activated catalyst based on coordination polymers of metals and bridging bidentate diolefin ligands.

Silver olefin complexes of the type $[Ag(olefin)_3][SbF_6]$ have been demonstrated to be amongst the most efficient initiators for EB curing of epoxy resins [4]. We have investigated the corresponding coordination polymers of coinage metal salts with diolefin linkers of the type $\{[M(diolefin)_{1.5}]X\}_n$ (M = Cu, Ag, Au, X = BF_4, PF_6, SbF_6, $B(C_6H_5)_4$) as catalyst precursors for the catalytic cationic polymerization of epoxides in autonomous self-healing composite materials. Metal centers, counter ions and linkers can be easily tuned in order to adapt to the specific requirements of the epoxy monomer and the curing process. The polymeric nature of the catalyst precursor ML_n (latent catalyst) allows mechanical activation of the precursor via removal of one olefin ligand to yield active, coordinatively unsaturated catalyst ML_{n-1}. Spacers based on the structural motif of Bisphenol A allow entanglement with the composite host matrix during the curing process which increases susceptibility towards activation by physical impact.

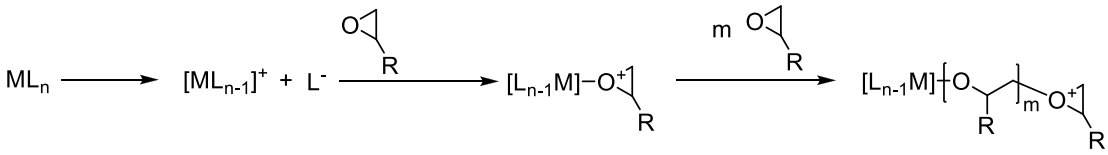

Figure 1: Catalytic cationic ring-opening polymerization of epoxides using coordinatively unsaturated metal complexes

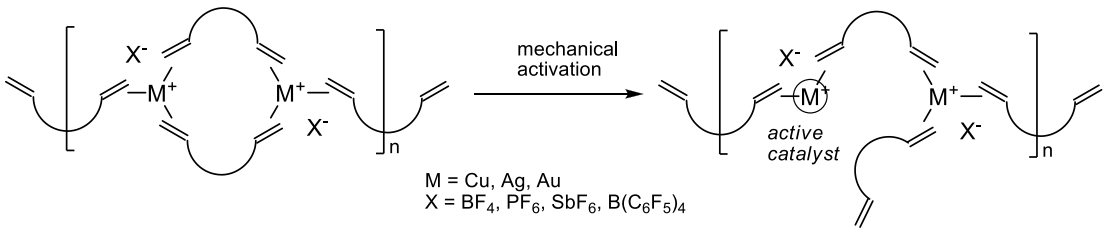

Figure 2. One-dimensional coordination polymer of coinage metal olefin complexes. Coordinatively fully saturated [M(olefin)$_3$] complex constitute the latent catalyst (left), whereas their coordinatively unsaturated counterparts [M(olefin)$_2$] after mechanical activation constitute the active catalyst (right).

The synthesis of these systems and preliminary testing in the context of self-healing will be reported. Comparison with related non-linked olefin ligand species and 'ligand-free' complexes will be made.

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