

Synthesis of Heterometallic Rare Earth-Zinc Aryloxido Complexes for Catalytic Applications

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Over the past three decades, heterometallic rare earth metal-zinc coordination compounds have gained attention as valuable molecular materials due to their remarkable magnetic, photochemical, catalytic, and structural characteristics [1-4]. The synthesis of RE^{III}-Zn^{II} complexes presents a promising approach to enhancing catalytic performance, offering improved reaction efficiencies and selectivity in various chemical transformations. In polymer and resin synthesis, these complexes can facilitate controlled polymerization processes, leading to advanced materials with tailored properties such as enhanced stability, mechanical strength, or thermal resistance.

In our work, we developed a simple synthetic route to RE^{III}-Zn^{II} coordination compounds by reacting homoleptic or heteroleptic zinc aryloxides, [Zn₄(sal-Me)₈] and [Zn₄(μ₃-OMe)₂(sal-Me)₆] (Hsal-Me = methyl salicylate) with 2 equiv of RECl₃ [5]. Depending on the zinc aryloxide precursor used, the formation of either trinuclear heterometallic clusters [REZn₂(sal-Me)₄Cl₃(H₂O)] (RE^{III} = Y, Ho, Er) using the first one or hexanuclear clusters [RE₂Zn₄(μ₃-OH)₂(μ-OMe)₂(sal-Me)₆Cl₄] (RE^{III} = Y, Ho, Er) using the second one was observed. The catalytic activities of homometallic and heterometallic compounds were investigated in the ring-opening polymerization (ROP) of pentadecanolide (PDL) and hexadecanolide (HDL), leading to the synthesis of low molecular weight materials, as pictured in Fig. 1.

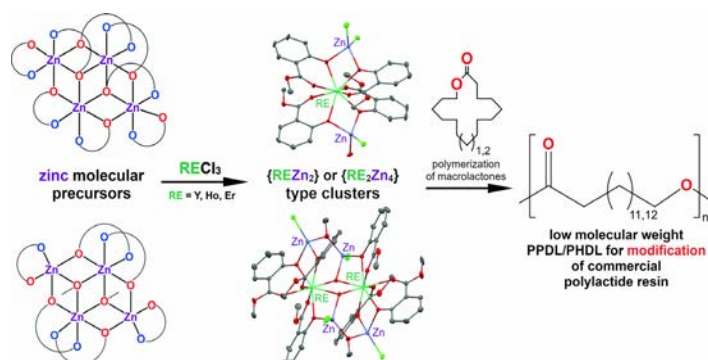


Figure 1. Synthesis of {REZn₂} and {RE₂Zn₄} type clusters for polymerization of macrocyclic lactones.

The low molecular weight polyesters (PPDL and PHDL) were examined as modifying agents for commercial polylactide resin (PLLA 2003D) and used to create PLLA/PPDL and PLLA/PHDL blends. Incorporating PPDL or PHDL into PLLA expanded its cold crystallization exotherm, increased its T_{cc}, hindered PLLA crystal growth, and resulted in reduced thermal stability and faster degradation. Currently, we are working on using the obtained complex compounds in the synthesis of alkyd resins.

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