Catalytic Activity and Magnetic Properties of Lanthanide Phosphates

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Lanthanide Ziegler-Natta (ZN) type catalysts are efficient catalysts for the stereospecific polymerization of dienes. However, these catalysts are poorly soluble in organic solvents and fail to polymerize polar vinyl monomers because these polar monomers deactivate them producing polymers with high polydispersity index (PDI). Therefore, neodymium-based ZN catalysts, $[Nd(\mu\text{-}DEP)_3]_x$ (DEP = diethyl phosphate), $NdCl_3.3TEP$ (TEP = triethyl phosphate), and (TEHP = tris(2-ethylhexyl) phosphate) were developed using the ligand exchange method during azeotropic distillation in a nitrogen environment for the polymerization of dienes as well as polar vinyl monomers such as methyl methacrylate (MMA), methyl acrylate (MA), and vinyl acetate (VA), in combination with triisobutylaluminum (TIBA) as a cocatalyst or in the presence of benzyl alcohol as an initiator. Adding an organic ligand and an electron donor improves the solubility of these catalysts while preserving stereospecificity, as $NdCl_3.3TEP$ showed 106 Kg polymer Nd^{-1} h^{-1} catalytic activity.

Previous studies have shown that halide or pseudohalide, either from the catalyst directly or from an external source, is necessary for polymerization to proceed successfully in ZN catalytic systems. To the contrary, $[Nd(\mu\text{-}DEP)_3]_x$, a novel halide-free Nd catalyst, polymerized bio-based β-myrcene with high stereospecificity (96% *cis*-1,4 content) and a narrow PDI (1.8). Additionally, $NdCl_3.3TEP$ was capable of homopolymerizing the dienes (isoprene and β-myrcene) with narrow PDI (1.6) and high *cis* stereospecificity (92% and 96%), respectively.

Comparing anionic, cationic, and radical polymerization techniques, these catalytic systems were employed successfully to polymerize ε-CL and γ-functionalized ε-CL with decreased sensitivity to substituents in ε-CL. Moreover, they performed better than the traditional catalysts: $Sn(Oct)_2$ and $Al(o\text{-}i\text{-}pr)_3$, in the polymerization of functionalized ε-CL with an ester linkage at the γ-position. $NdCl_3.3TEP$ and $NdCl_3.3TEHP$ synthesized both poly ε-caprolactone (PCL) and poly $^\gamma$-functionalized ε-CL with a variety of linkages at the γ-position, including benzyl, 4-phenyl butyrate, acetate, bromo, and γ-2-[2-(2-methoxyethoxy)ethoxy]ethoxy (ME₃) with narrow PDI (1.22 - 1.84). According to kinetic studies, the TEP ligand reacted with ε-CL at a lower rate than the bulkier TEHP ligand.

Based on kinetic studies and the effective synthesis of block copolymers such as poly (β-myrcene)-*b*-poly (isoprene), poly (β- myrcene)-*b*-PMMA, PVL-*b*-PCL (PVL = polyvalerolactone), PBrCL-*b*-PCL, PME₃CL-*b*-PCL, and P(ε-CL)-*b*-P(L-lactide), all our synthesized catalytic systems demonstrated the *quasi-living* behavior. Our research allowed us to show the capacity of a single catalytic system for the polymerization of lactones, both non-functionalized and functionalized lactones, in addition to dienes and vinyl monomers.

Furthermore, after analyzing the crystal structure of $([Nd(\mu\text{-}DEP)_3]_n$ obtained from single crystal XRD, that showed the bridging phosphate groups with distorted tetrahedrons connect the neighboring 6-coordinated Ln^{3+} metal ions, eventually forming one-dimensional polymeric chains. The neighboring Ln^{3+} ions are spaced widely in the same polymeric chain that may act as separate magnetic domains. Thus, two isomorphic lanthanide organophosphate coordination polymers (LOCPs) using Nd and Gd metal ions: $([Nd(\mu\text{-}DEP)_3]_n$, and $[Gd(\mu\text{-}DEP)_3]_n)$ were synthesized using the azeotropic distillation method, and were investigated for the magnetic properties using SQUID magnetometer. The magnetic studies showed superparamagnetic behavior in these compounds with a magnetic moment and cluster density for $[Nd(\mu\text{-}DEP)_3]_n$ are 2.66 μ_B and 3.28 $\times10^{20}$ /cm³, and that for $[Gd(\mu\text{-}DEP)_3]_n$ compounds are 8.12 μ_B and 1.71 $\times10^{21}$ /cm³ respectively estimated from the Langevin fitting, which closely agrees with the theoretical values. The study shows these compounds are very promising to be used as Single Chain Magnets and might be helpful for high-density data storage devices in the future.

$$NdCl_3.6H_2O \ + \ 3RO\text{-}P(=O)(OR)(OR) \xrightarrow[\text{azeotropic distillation}]{\text{toluene, ethanol}} NdCl_3 \text{---} 3\ RO\text{-}P(=O)(OR)(OR)$$

R = TEP, TEHP