

Editorial

Catalysis in Plastics for the 21st Century

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For this Special Issue, which is part of the Organic and Polymer Chemistry Section, we would like to present the following editorial message. The Special Issue accepted manuscripts related to molecular catalysis, including metal-catalyzed polymerization of α -olefins, ring opening polymerization (ROP) of cyclic esters, acyclic diene metathesis polymerization, mechanistic studies, co-catalyst effects and DFT calculations. In this Special Issue, there is one review entitled “Synthesis of Biodegradable Polymers: A Review on the Use of Schiff-Base metal Complexes as catalysts for the Ring Opening Polymerization (ROP) of Cyclic Esters” [1]. As expected from the beginning, the scope of the catalysts covered in this issue is broad, from zirconium and hafnium to iron and cobalt-based catalysts.

For example, the Special Issue summarizes efforts in the area of homogeneous catalysts concerning iron catalysts containing bis(arylimino)tetrahydrocyclohepta[*b*]pyridine ligands applied to the polymerization of ethylene. The structure/activity revealed that the activity dropped as the *ortho*-cycloalkyl ring size increased; polymer molecular weights were also found to be related to the *ortho*-cycloalkyl ring size [2]. DFT calculations on neutral and cationic bis(imino)pyridine iron and cobalt systems have been employed to shed light on the nature of the active species and *modus operandi* of the polymerization system. The results revealed that the reactivity was more closely associated with valence electron numbers rather than charge numbers. Moreover, an electron was found to be lost from the ligand set rather than the metal, with the metal retaining an oxidation state of +2 for the duration of the process [3]. DFT calculations have also been conducted on systems involving acyclic and cyclic MAO species and also their complexation with $[L(R)_2FeCl]^+$ (L = pyridine-2,6-diylidimethanimine; R = Me, Ph). The data demonstrated the presence of intramolecular O-to-Al dative bonding for the cyclic species, which resulted in the latter being a much better ligand for the iron complexes of interest [4]. α -Diimine-type ligation at Zr and Hf, in which there is a camphor backbone in the chelate ligand, has been employed in ethylene/1-octene copolymerization. Ultrahigh molecular weight products were obtained from catalysis runs with Zr conducted at 120 °C and 3 MPa ethylene, while Hf complexes were virtually inactive [5]. The remaining two contributions to this Special Issue focus on alternatives to petroleum-based polymers. Acyclic diene metathesis (ADMET) polymerization, conducted in the presence of a Ru-carbene catalyst, followed in tandem by hydrogenation using a small amount of Al₂O₃. The copolymerizations employed dianhydro-*D*-glucityl bis(undec-10-enoate) and 1,9-decadiene, and under the conditions employed (H₂ 1.0 MPa, 50 °C) high molecular weight unsaturated polyesters were afforded [6].

Moreover, this Special Issue introduces efforts concerning ring opening polymerization using air- and moisture-stable polymetallic Ti and Zr complex catalysts [7]. In these systems, the ligation involved amine bis(phenolates) into which an amino acid functionality had been incorporated, i.e., amino acid ethyl ester-derived bis(phenolate) ligands. The aggregate size was controlled by the steric bulk of the pendant arm. In the ROP of *rac*-lactide, faster rates were observed for binuclear (versus tetranuclear) Ti complexes, whilst for Zr, a trimetallic derivative revealed the best control over tacticity.



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Finally, we would like to express our sincere thanks to those who submitted articles of such high quality to this Special Issue. We hope that you the readers can also enjoy this Special Issue.

Conflicts of Interest: The authors declare no conflict of interest.

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