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Editorial

Molecular Catalysis for Precise Olefin Polymerization and ROP 2015

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1. Background

The growth of emerging markets, particularly in the Far East, has fuelled the demand for new plastic materials. This in turn has stimulated both academic and industrial interest in the design of catalyst systems for which new Intellectual Property (IP) can be generated, and in new polymeric materials possessing desirable properties such as biodegradability.

Underpinning much of the work is synthetic chemistry and, in particular, ligand-set design. The ability to tune the electronic and steric properties of the resultant metal catalysts and thereby influence both the catalytic activity, as well as the resultant polymer properties, is proving particularly fruitful. Traditionally, early transition metals have been employed particularly for polyolefin synthesis, but in recent years late transition metals have emerged as intriguing alternatives, and each are attracting industrial interest [1]. For ring opening polymerization systems, catalysts incorporating elements from many parts of the periodic table are showing promise [2].

In this Special Issue, manuscripts focusing on aspects of new catalyst systems for the homo- or co-polymerization of α-olefins, on the ring opening polymerization (ROP) of ε-caprolactone, and on co-polymerizations involving CO_2/cyclohexene oxide are presented [3–8]. This work will be of immense interest to those involved in catalyst design, organometallic chemistry and polymer synthesis.

2. The Present Issue

I would like to thank all of the authors and reviewers for contributing to this special issue, which together makes an excellent collection of works. Furthermore, I would like to thank Mary Fan and her editorial team for their sterling efforts in putting this issue together and the Editor-in-Chief Keith Hohn.

This issue comprises six research papers (articles).

- In the first contribution, Solan and coworkers have employed bulky 2-imino-6-(1-napthyl)pyridine ligation at aluminium, and have studied the impact of employing N bound aryl groups bearing *para* substituents with differing electronic properties on the ROP ofε-caprolactone. Upon activation with benzyl alcohol, the system employing the electron donating *i*Pr group at the *para* position proved to be the most active, for example at 100% conversion was achieved at 50 °C over 1 h. However, given the bromide derivative was move active that that containing a *para*-hydrogen, the rate of polymerization is thought to be determined by a number of factors including alkoxide nucleophilicity and the Lewis acidity at the metal [3]. The related 2-(Phenyl-2-olate)-6-(1-amidoalkyl)pyridine dimethylaluminium complexes have also shown promise in the ROP of ε-caprolactone [9].
- In the second paper, Huang and coworkers studied the use of group IV (Ti, Zr) complexes incorporating *N*,*P*-chelate ligation of the diisopropylphosphorus-phenylamine type. Upon activation with MAO, high activity was observed for both the polymerization of ethylene and the copolymerization of ethylene/*N*-acetyl-*O*-(dec-9-enyl)-L-tyrosine with high co-monomer

incorporation (2.56 mol%) for the latter case. The molecular weights associated with the copolymers were somewhat lower than those of the homopolymers [4].

- In the third paper, our laboratory continued our investigations into the coordination chemistry (and resultant catalytic properties) of bulky bi-phenols of the type 2,2′-RCH[4,6-$(tBu)_2C_6H_4OH]_2$ (R = Me, Ph), tri-phenols 2,6-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4-methylphenol and tetra-phenols α,α,α/,α/-tetrakis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*p*- or –*m*-xylene [10,11]. In this contribution, we focus on bis(imido) molybdenum(VI) complexes and report on their ability to ring open polymerize ε-caprolactone. Reasonable activity was only achievable at temperatures of 100 °C or more over time periods of at least 1 h [5].
- In the fourth article, Michiue, Mitani and Fujita of the Mitsui Chemical Corporation studied substituent effects when using activated *rac*-$[Me_2Si(Indenyl')_2]ZrCl_2$ (where Indenyl′ is a generic indenyl grouping) on products containing pendant vinyls and vinylenes, which result from copolymerizations involving ethylene/1,3-butadiene or propylene/1,3-butadiene. Systems were identified which afforded copolymers with predominantly vinyl groups [6]. This work built on preliminary screening results for which it was found that catalysts inserting α-olefins via 1,2-insertion tend, particularly in the presence of steric regulation, to produce olefin/butadiene copolymers having pendant vinyl groups [12].
- The final two papers of this Special Issue are from the group of Darkwa. With Nazaki and coworkers, they have investigated the ability of bis(pyrazole)zinc(II) benzoates to act as catalysts for the copolymerization of CO_2 with cyclohexene oxide. Such systems were found to be active without the need for a co-catalysts and could operate at low CO_2 pressures (1.0 MPa). Copolymers with high carbonate content (⩽98%), low to moderate molecular weight (<12300 g/mol) and with glass transition temperatures suggestive of alternating copolymers were isolated. Highest observed catalytic activity was achieved when employing catalysts with high electrophilicity at the metal, specifically derivatives bearing 3,5-dinitrobenzoates and 2-chlorobenzoates [7]. The second Darkwa contribution describes a number of iron(III) complexes for 1-hexene polymerization and extends their work on tridentate *O*,*N*,*N*-phenoxysalicylaldimine containing complexes [13]. Upon activation with $EtAlCl_2$, these systems afforded low molecular weight poly(1-hexene) with branched microstructures; the presence of dominant longer branches were indicative of 2,1-insertion of the monomer. Single–site behaviour was observed for these catalysts over a variety of catalytic conditions [8].

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