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14. ABSTRACT

This Advances in Olefin Polymerization Catalysis symposium was held at the 247th ACS National Meeting and Exposition, March 19, 2014 in Dallas, Texas and consisted of twelve (12) invited/contributed talks. The hosting ACS division was the Division of Catalysis Science and Technology (CATL), and the specific objective of the symposium was to provide a unified, inclusive platform for the dissemination of results pertaining to polyolefin research. This was the only symposium dedicated exclusively to polyolefins and provided an opportunity for colleagues from academic institutions, national laboratories, and industry to connect and exchange ideas by which

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Report Title

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Number of Papers published in peer-reviewed journals:

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Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Brian K. Long	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
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Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

FINAL REPORT

Request for Symposia Support: Advances in Olefin Polymerization Catalysis

Brian K. Long
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

A. Summary of Proposal

The field of olefin polymerization is driven by the ever-increasing demand for polyolefins with tailored mechanical and physical properties, and persists at the cutting edge of scientific research. To highlight these efforts, the *Advances in Olefin Polymerization Catalysis* symposium was proposed as a venue to present recent progress in the design and development of innovative catalysts for polyolefin synthesis. Specific topics of interest included, but were not limited to, heterogeneous catalysis, homogeneous catalysis, advances in catalyst activation, methods for polymer topological control, mechanistic and kinetic investigations, and distinctive polymeric materials produced via catalytic olefin polymerization. This proposal requested support to offset expenses incurred by invited speakers to the *Advances in Olefin Polymerization Catalysis* symposium through the Army Research Office's Conferences and Symposia Grants program.

B. Summary of Conference

This *Advances in Olefin Polymerization Catalysis* symposium was held at the 247th ACS National Meeting and Exposition, March 19, 2014 in Dallas, Texas and consisted of twelve (12) invited/contributed talks. The hosting ACS division was the Division of Catalysis Science and Technology (CATL), and the specific objective of the symposium was to provide a unified, inclusive platform for the dissemination of results pertaining to polyolefin research. This was the only symposium dedicated exclusively to polyolefins and provided an opportunity for colleagues from academic institutions, national laboratories, and industry to connect and exchange ideas by which new collaborations may be established. In total we estimate that approximately 100 individuals attended this daylong symposia.

Wide ranges of topics were discussed in the symposium including: DFT investigations of Ziegler-Natta catalysts and how Lewis bases such as THF affect the polymerization process. Polyolefin architectures for energy-related applications were presented, with an emphasis on performance as capacitors and ion exchange membranes. Stereoengineering of polyolefin microstructures was described using a unique zirconium-amidine complex and an industrial contribution explored the modulation of MAO cocatalysts for improvement in catalyst activity for olefin polymerization. One presentation described work on bulky C_s symmetric catalysts for syndiotactic polypropylene. Several talks illustrated the synthetic utility of late-metal α-diimine complexes and their value for tailored polyolefins. Other PI's described some of their work with late-metals in an effort to incorporate polar comonomers into olefin architectures. Finally, two talks described the use of some unusual ruthenium catalysts for polyolefin synthesis. Overall, all talks were well received, a range of topics were discussed and both industrial and academic groups were represented. In sum, it was truly an exceptional one-day symposium, and we are extremely grateful to the Army Research Office for their support of this effort.

C. Chairpersons

The chairpersons/organizers for this symposium were:

- Brian Long, Asst. Professor, University of Tennessee, Long@utk.edu and
- Kevin Noonan, Asst. Professor, Carnegie Mellon University, noonan@andrew.cmu.edu

D. List of Presenters

- Prof. Zhibin Guan, University of California, Irvine
- Prof. Lawrence Sita, University of Maryland
- Prof. Richard Jordan, University of Chicago
- Prof. Steve Miller, University of Florida
- Prof. T. C. (Mike) Chung, Penn State University
- Prof. Olafs Daugulis, University of Houston
- Prof. Brian Long, University of Tennessee
- Prof. Kyoko Nozaki, University of Tokyo
- Dr. Min Li, Albemarle Corporation
- Mr. Mohammed Al-Hashimi, Texas A&M University at Qatar
- Mr. Tobias Friedberger, University of California, Irvine
- Dr. Philippe Sautet, University of Lyon

E. Agenda

- 8:20am – **Welcome Remarks**
- 8:30am – Olafs Daugulis
- 9:00am – Brian Long
- 9:30am – T.C. (Mike) Chung
- 10:00am – Kyoko Nozaki
- 10:30am – Lawrence Sita
- 11:00am – Tobias Friedberger
- 11:30am – **Lunch**
- 1:30pm – Philippe Sautet
- 2:00pm – Richard Jordan
- 2:30pm – Min Li
- 3:00pm – Zhibin Guan
- 3:30pm – Mohammed Al-Hashimi
- 4:00pm – Stephen Miller
- 4:30pm – **Closing Remarks**

F. Abstracts of Presentations

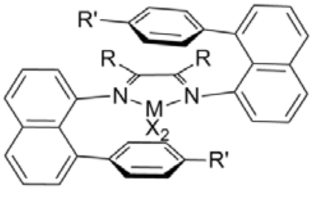
1. Olafs Daugulis

173 - Alkene polymerization by 8-arylnaphthyldiimine palladium and nickel complexes

Kate Allen[2], Kristine Klimovica1, Danfeng Zhang[2], Jesus Campos[2], Maurice Brookhart[2], Olafs Daugulis[1], olafs@uh.edu.

(1) Department of Chemistry, University of Houston, Houston, TX 77204-5003, United States, (2) Department of Chemistry, University of North Carolina-Chapel Hill, Chapel Hill, NC 27599-3290, United States

Nickel(II) and palladium(II) α-diimine complexes of general structure **1** possessing hindered 8-arylnapthylimino groups have been prepared and used for alkene polymerization. These catalysts possess increased axial bulk relative to standard ortho-disubstituted aryldiimine-metal complexes, which results in lower rates of chain transfer relative to chain propagation and thus higher polymer molecular weights and more narrow molecular weight distributions. The easy synthesis of 8-aryl-1-naphthylamines by carbon-hydrogen bond functionalization methodology provides ready access to this new class of α-diimine-based catalysts in which the 8-substituent is ideally positioned to provide steric bulk at the metal axial coordination sites. In addition to the polymerization studies, mechanistic features of the palladium and nickel diimine systems will be reported.



1

2. Brian Long

174 - Robust Ni(II) α-diimine catalysts for high temperature ethylene polymerization

Brian K. Long, Long@utk.edu, Jennifer L. Rhinehart, Lauren A. Brown.

Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States

A class of sterically-demanding NiII α-diimine precatalysts were synthesized utilizing 2,6-bis(diphenylmethyl)-4-methyl aniline. When activated with methylaluminoxane, the catalyst NiBr2(ArN=C(Me)-C(Me)=NAr) (Ar = 2,6 bis(diphenyl-methyl)-4-methylbenzene) was highly active, produced well-defined polyethylene at temperatures up to 100 °C (Mw/Mn = 1.09–1.46), and demonstrated remarkable thermal stability at temperatures typically encountered for industrially used gas-phase polymerizations (80-100 °C).

3. T.C. (Mike) Chung

175 - Synthesis of functional polyolefins for energy storage applications

T. C. Mike Chung, chung@ems.psu.edu,

Department of Materials Science and Engineering, The Pennsylvania State University, University park, PA 16802, United States

Polyolefins, including polyethylene (HDPE and LLDPE) ad polypropylene (PP), represent half of commercial polymers produced in the world. They are known to be cost-effective and good performing materials used in a broad range of commodity applications. Less attention has been paid to their specialty applications, commonly requiring the material with multiple performance functions. The limitations of polyolefins have stemmed from lack of functionality and structure diversity. On the other hand, functionalization of polyolefins these days, to a large extent, still remain a scientifically challenging and industrially important research area. Both direct and post-polymerization approaches have been extensively studied but met with limited industrial success. In the past two decades, in conjunction with advances in single-site metallocene catalysis, a new method based on the "reactive" polymer approach has emerged, which affords a new class of functional polyolefins with high molecular weight and well-controlled molecular structures that have functional groups located at chain ends, side chains, and block/graft segments. In this paper, I will discuss the specific catalyst systels with the polymerization mechanisms that allow the incorporation of designed comonomers and chain transfer agents in the desirable functional polyolefin structures without side reactions. Some of them show distinctive multiple phase morphology with sharp hydrophobic-hydrophilic microphase separation and surface properties, they offer excellent response to polarization and ion conductivity, etc. They present potentials for polyolefins in high-value, specialty applications. In this presentation, I will discuss two energy-related applications, including polymer film capacitors for energy storage and ion exchange membranes for electrochemical devices, to discuss the effects of functional polymer structures on their performances.

4. Kyoko Nozaki

176 - Steric effect of ligands in the late-transition metal catalyzed olefin/polar monomer copolymerization

Kyoko Nozaki, nozaki@chembio.t.u-tokyo.ac.jp,

Department of Chemistry and Biotechnology, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

Group 10 metal complexes bearing phosphine-based ligands have been reported to catalyze the copolymerization of ethylene with various polar vinyl monomers. Here in this presentation, steric effect of substituents on the phosphorus atom will be quantitatively evaluated in relation to the catalytic activity, molecular weight, and incorporation ratio of polar monomers. Palladium complexes of phosphine–sulfonate and bisphosphine monoxide will be mainly discussed.

5. Lawrence Sita

177 - Dynamic two-state coordinative chain transfer living polymerization and the stereoengineering of polyolefin microstructure

Lawrence R. Sita, lsita@umd.edu,

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States

As the demand for new polymeric materials with superior performance properties that can be used to support existing, new, and yet-to-be discovered technologies continues unabated, new paradigms are required that have the potential to dramatically change the range and pace at which olefin commodity feedstocks can be converted into new classes of polyolefins, hydrocarbons and specialty chemicals of commercial and societal value. This talk will focus on our efforts to expand the available set of 'tools' that can be wielded in programmed fashion to produce a near continuum of different polyolefin materials that exist between two different limiting stereochemical microstructures, co-polymer compositions or polymer architectures – all from a single catalyst and with a high degree of precision. When combined with living coordinative chain transfer polymerization (LCCTP) that employs an excess of a main group metal alkyl as 'surrogate' chain growth sites, practical (> kilograms) quantities of a vast array of new polyolefin materials with unique (micro)structures and technologically-interesting properties are now available to support a new period of discovery and innovation.

6. Tobias Friedberger

178 - Ruthenium complexes for olefin insertion polymerization

Tobias Friedberger, tfriedbe@uci.edu, Zhibin Guan.

Department of Chemistry, University of California Irvine, Irivine, California 92697-2025, United States

Polyolefins like polyethylene and polypropylene are produced on a million ton scale and comprise a large portion of commercial polymeric materials. Their widespread application is based on high cost efficiency (cheap monomer and highly active catalysts) and the accessibility of different polyolefin grades from the same monomer (i.e. HDPE vs. UHMWPE) by simply changing the catalyst. Despite this success, the development of novel transition metal olefin polymerization catalysts is still of great interest. Late transition metals, due to their higher functional group tolerance, are able to produce functionalized polyolefins via direct copolymerization of polar vinyl monomers and non-polar olefins. Ruthenium has been used for a variety of catalytic reactions involving olefins (i.e. hydrogenations, metathesis) and showed excellent functional group tolerance, making it a seemingly promising candidate. However, Ru based olefin insertion polymerization catalyst are scarce, but our lab has recently demonstrated ethylene polymerization by an active Ru center. Here, the synthesis, characterization, and ethylene polymerization behavior of novel mononuclear Ru(OPO)(PPh3)(L) (*OPO* = bisanionic phosphine ligand, L = PPh3 or MeCN) complexes will be disclosed. The Ru(II) precursors were activated with solid methylaluminoxane at elevated temperatures to give linear (< 10 Me / 1000C), semicrystalline (Tm = 120 – 135°C) polyethylene with one of the highest reported activity for Ru based catalysts. Several novel electronic and steric ligand variants were prepared and it was found that the polymerization activity increased with the electron withdrawing character of the ligand. Furthermore, copolymerization reactions of ethylene with α-olefins and polar monomers were also investigated.

7. Philippe Sautet

195 - Tetrahydrofuran in TiCl4/THF/MgCl2: A non-innocent ligand for supported Ziegler-Natta polymerization catalysts

Philippe Sautet[1], Philippe.Sautet@ens-lyon.fr, Etienne Grau[3], Anne Lesage[4], Sebastien Norsic[3], Christophe Coperet[2], Vincent Monteil[3].

(1) Ecole Normale Superieure de Lyon and CNRS, University of Lyon, Lyon, France,
(2) Department of Chemistry, ETH Zurich, Zurich, Switzerland,
(3) Univ. Lyon 1, CPE Lyon, CNRS, Chimie Catalyse Polymères et Procédés, University of Lyon, Lyon, France,
(4) CNRS, Ecole Normale Supérieure de Lyon, Centre de RMN à Très Hauts Champs, University of Lyon, Lyon, France

While Ziegler-Natta (ZN) polymerization is one of the most important catalytic industrial processes, the atomic-scale nature of the catalytically active surface species remains unknown. Coupling high-resolution solid-state NMR spectroscopy with periodic DFT calculations, we show the influence of the Lewis base Tetrahydrofuran THF and demonstrate that the major surface species in the Ziegler-Natta pre-catalyst corresponds to an alkoxy Ti(IV) surface species, which probably results from the ring opening of THF on a cationic Ti(IV) species. The stability of THF on the precatalyst and the reaction pathways are probed by the DFT calculations, and by combination with NMR, the nature of surface species is demonstrated. Alcohol additives lead to similar surface species.

8. Richard Jordan

196 - Electronically unsymmetrical catalysts for the copolymerization of olefins with polar vinyl monomers

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Department of Chemistry, University of Chicago, Chicago, IL 60637, United States

The development of catalysts that incorporate polar CH2=CHX monomers in olefin insertion polymerizations would enable the direct synthesis of functionalized plastics. (*Ortho*-phosphino-arenesulfonate)PdRL catalysts copolymerize ethylene with alkyl and aryl vinyl ethers to linear copolymers containing up to 15 mol % vinyl ether. The (PO)PdR catalysts also copolymerize ethylene and vinyl fluoride. Mechanistic studies confirm that these materials are true copolymers, rule out ionic and radical polymerization mechanisms, and support insertion polymerization mechanisms. Relative binding strengths and insertion rates for ethylene and vinyl ethers measured with a model (PO)PdR catalyst, (2-P(3,5-(CF3)2)-Ph)2-4-Me-benzenesulfonate)PdMe by low T NMR accurately predict vinyl ether incorporation levels in ethylene polymerization. New (phosphine-bis-sulfonate)PdR catalysts that self-assemble into tetranuclear arrays and produce ultra high molecular weight linear polyethylene and incorporate higher levels of vinyl fluoride have been developed. The electronic asymmetry associated the

phosphine-sulfonate ligands in (PO)PdR catalysts appears to be important for their function and new families of catalysts with electronically unsymmetrical ligands including NHC-sulfonates, phosphine-borates and phosphine-phosphonates are being explored. The reactivity of anionic [(PO)PdR2]- species will also be discussed.

9. Min Li

197 - Improving activation efficiency of non-alkylated single-site catalysts by methylaluminoxane (MAO) for olefin polymerization

Min Li, min.li@albemarle.com, Steve Diefenbach.

Performance Catalyst Solutions, Albemarle, Baton Rouge, LA 70805, United States

Methylaluminoxane (MAO) containing residual TMA can serve to both alkylate/activate metallocene dichloride precatalysts for olefin polymerization. Often this requires the inefficient use of a large excess of MAO. Recent experimental evidence has suggested a refined picture for the MAO activation process of metallocenes. Built upon this evidence and better understanding of the overall MAO activation mechanism, new generations of modified supported MAO-based single-site catalysts are being developed which exhibit significantly improved catalyst productivity compared with conventional supported MAO-based catalysts. Furthermore, this improvement can be accomplished without sacrificing the activated metallocene's ability to control desirable polymer properties like molecular weight or it's reactivity towards comonomer.

10. Zhibin Guan

198 - Ruthenium-based catalysts for olefin insertion polymerization

Zhibin Guan, zguan@uci.edu,

Chemistry, University of California, Irvine, Irvine, CA 92697, United States

One major research thrust in our lab is to develop new transition metal catalysts that can polymerize simple olefins into new functional materials at high efficiency and atom economy. Previously we have worked extensively with late transition metals, Pd(II) and Ni(II)-based complexes for olefin insertion polymerization. Recently, we have shifted our effort to the central part of the periodic table and particularly focused our attention on ruthenium metal. Situated right in the middle of the transition metal block, ruthenium may potentially be able to combine high activity with good functional group tolerance. Despite this promising, there are extremely rare examples of Ru-based catalysts for olefin insertion polymerization. For the very reported systems, none has unambiguously established that the Ru metal is the active catalytic center. Our lab has recently designed an arene-tethered ruthenium complex (η6-C6H5(CH2)3SCH3RuCl2) and show that it can catalyze ethylene polymerization upon activation with AlMe2Cl. For mechanistic studies, we synthesized the homologous dimethylated η6-C6H5(CH2)3SCH3Ru(CH3)2 complex, which upon activation with the Brookhart acid ([H(Et2O)2]+ [BAr'4]-) was also active for ethylene insertion polymerization. 1H NMR and mass spectrometry (MS) studies provide direct evidence for a ruthenium cationic [η6-C6H5(CH2)3SCH3Ru(oligomer)]+ complex as the active species during polymerization. This has ambiguously shown for the first time a ruthenium complex as the active species for catalyzing olefin insertion polymerization. Following this initial success, we have successfully developed a few other Ru complexes that are active for ethylene insertion polymerization. Some complexes are also capable of copolymerizing ethylene with polar olefins. In this presentation, I will discuss our ligand and catalyst designs, mechanistic studies, and polymerization studies.

11. Mohammed Al-Hashimi

199 - Phase-separable PIB polymerization catalysts

Mohammed Al-Hashimi[1], mohammed.al-hashimi@qatar.tamu.edu, Hassan H. S Bazzi1, David D. E Bergbreiter[2].

(1) Department of Chemistry, Texas A&M University at Qatar, Doha, Qatar,
(2) 2Department of Chemistry, Texas A&M University, Texas, United States

"Green chemistry" is a central issue, in both academia and industry, with regard to chemical synthesis in the 21stcentury. With the widely accepted drive towards more sustainable technologies, there is an urgent need for developing cleaner Sustainable Concepts in
Olefin Metathesis. Olefin metathesis has emerged as a powerful tool in C-C double bond formation in the last decade having numerous applications in polymer chemistry and material science. Ruthenium-based catalysts are commonly used in organic synthesis, mainly in olefin metathesis reactions. Ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM), in particular are versatile methods for the synthesis of functional polymers. Grubbs and Hoveyda-Grubbs catalysts are certainly the most popular ruthenium- based complexes in this field. Unfortunately, only a limited number of studies have been conducted where both recycling and ruthenium waste content are examined. Moreover, numerous papers do not report on the levels of contamination in the product, which clearly is a drawback when developing olefin metathesis for industrial practice. The separation of the polymeric product and the catalyst is one of the major challenges facing metathesis polymerization. This process currently requires extra steps or additional chemical processes. Alternative processes that avoid a second process step thus remain of interest. Our approach uses a scheme in which the solubility of the Ru catalyst byproducts is differentiated from the solubility of the product polymer. This strategy employs soluble polymer-bound NHC-ligated Ru catalysts that use polyisobutylene-containing NHC ligands and a liquid/liquid biphasic separation of catalyst residues from polymer products after a reaction. The catalytic activities of the supported Ru–carbene complex in ROMP are comparable to those of their homogeneous counter- parts. The separability of these catalysts leads to lower Ru contamination (167 ppm levels) in the polymer products in comparison to the nonsupported Hoveyda-Grubbs catalyst (4764 ppm).

12. Stephen Miller

200 - Single-site catalysts for increasing the branch content of polyolefins

Ha T. H. Nguyen, Nicole L. Gibbons, Stephen A. Miller, miller@chem.ufl.edu.

Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

Several sterically expanded single-site catalysts exhibit an unusual activity toward alpha-olefins versus ethylene. This proclivity has allowed the construction of novel ethylene/alpha-olefin copolymers, most recently novel ethylene/propylene copolymers. Also demonstrated is the production of branched polyethylene from ethylene alone, either via a chain reincorporation mechanism, or via multi-catalyst strategies. These novel polymers will be compared and contrasted with those available from catalysts with conventional behavior.