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COVER SHEET FOR PROPOSAL TO THE NATIONAL SCIENCE FOUNDATION

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TITLE OF PROPOSED PROJECT **International Collaboration in Chemistry: New polyolefin architectures via advanced catalysts and customized chain control agents**

REQUESTED AMOUNT	PROPOSED DURATION (1-60 MONTHS)	REQUESTED STARTING DATE	SHOW RELATED PRELIMINARY PROPOSAL NO. IF APPLICABLE
$ **785,671**	**36** months	**09/01/10**	**1007180**

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PI/PD DEPARTMENT **Materials and Chemical Engineering**	PI/PD POSTAL ADDRESS **P.O. Box 210012** **Cincinnati, OH 452210012** **United States**
PI/PD FAX NUMBER **513-556-2569**	

NAMES (TYPED)	High Degree	Yr of Degree	Telephone Number	Electronic Mail Address
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CERTIFICATION PAGE

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COVER SHEET FOR PROPOSAL TO THE NATIONAL SCIENCE FOUNDATION

FOR CONSIDERATION BY NSF ORGANIZATION UNIT(S) - continued from page 1
(Indicate the most specific unit known, i.e. program, division, etc.)

CHE - CHEMICAL MEASUREMENT & IMAGING
CHE - CHEMICAL SYNTHESIS

International Collaboration in Chemistry:

New polyolefin architectures via advanced catalysts and customized chain control agents

Intellectual Merit: Polyolefins are the dominant polymeric material used in a variety of commercial applications chiefly due to the versatility of their properties associated with control over chemical microstructure and the flexible processing that these structural modifications enable. For example, highly linear and high molecular weight polyolefins can be processed through gel spinning to produce fibers used to produce bulletproof vests while controlled short chain branching can lead to low crystallinity materials for ideal thermoplastic elastomers competitive with siloxanes in some applications. Chemical microstructure and processing jointly control the morphology of nano-structured crystals in polyolefins. Rapid progress in polyolefin synthesis has been driven by catalytic control over molecular weight, molecular weight distribution and modality, tacticity and comonomer incorporation. However, compared to advances in the synthesis of copolymer topologies in anionic polymerizations, the control of microstructure in polyolefins is relatively rudimentary. This proposal will develop cost-effective methods to develop well-defined multi-block polyolefins with controlled placement of functionality and branching. The approach will utilize new catalysts as well as customized chain-transfer agents. To quantify and assess developments in polyolefin microstructure, novel methods for the characterization of the topology of complex macromolecular structures and complexes will be developed. A novel characterization method using neutron scattering will be coupled with more traditional chromatographic, rheological and light scattering methods to complete the synthesis-structure-property relationship for development of novel polyolefin nanostructures.

Broader Impact: The proposed work involves significant interaction with LyondellBasell which is the top producer of polyolefins and with whom both the PI and the Russian PI have had previous interactions. A post-doc will primarily work in Moscow with frequent visits to Cincinnati, Frankfurt and Ferrara, Italy. The post-doc will interact with a broad range of scientist from his main exposure to synthesis in Moscow, high throughput synthesis in Frankfurt and commercial scale-up in Ferrara, Italy and Cincinnati as well as neutron scattering and characterization techniques in Cincinnati and at national user facilities in the US. The project also involves an undergraduate REU student and a graduate student who will travel to Moscow and Frankfurt as well as to national user facilities in the US for neutron scattering measurements. A RET high school teacher will travel to Moscow State University for one month per year to work on catalyst synthesis and to participate in an existing high school teacher program at the Russian university. These interactions will broaden scientific interactions with Russia as well as develop a diverse, globally-engaged, US science and engineering workforce. The project will select where possible minority and women participants for the participating students and teacher. The PI has a track record of engaging minorities and women in similar REU and RET projects. A new web based course on novel polyolefin materials will be added to the PI's web suit of courses that averages over 70 independent hits per day.

Value Added of the Proposed International Collaboration: Prof. Ilya Nifant'ev is an expert in organic and organometallic synthesis and he will lead the development of new catalysts and chain transfer agents. The post-doc will primarily work with Prof. Nifant'ev in Moscow. The collaboration also offers unfunded participation by four research scientists at LyondellBasell Corporation who will offer expertise in industrial catalyst development, high-throughput polymerization techniques and polyolefin characterization. Coupled with the PI's expertise in polyolefin characterization and development of novel analytic methods using neutron scattering the team is ideally suited to address the development of novel polyolefin architectures using advanced catalysis and group transfer agents. The proposed work will initiate a new interaction between Moscow State University and the University of Cincinnati.

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Appendix Items:

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1. PROJECT DESCRIPTION

1.1 Background and Problem Statement

Polyolefins are attractive due to their low cost and wide range of applications. Because they are commodity thermoplastics, improvements in polyolefin properties and performance significantly benefit society. We continue to witness remarkable progress in this area, mostly due to new catalysts that allow better control of polyolefin microstructure (molecular weight, molecular weight distribution, co-monomer incorporation, and tacticity). [1-6] However, cost-effective ways to assemble more advanced supramolecular structures (i.e., well-defined multi-block polymers with controlled placement of functional groups and branching) with inexpensive olefin monomers remain elusive. We propose to develop synthetic approaches to these advanced polyolefins. Polymerization methods that combine new catalysts and customized chain-transfer agents will be explored collaboratively in Prof. Nifant'ev's lab at the Moscow State University. Coincidentally, Prof. Beaucage will develop techniques to characterize the new polymers and understand how they self-assemble in solution or in the solid state. The project will also involve interaction with LyondellBasell through implementation of these new catalysts in high-throughput experiments in Frankfurt, Germany in collaboration with Dr. Kirsten and using computational techniques with Dr. Nagy in Cincinnati, as well as development of new polyolefins using these catalysts systems at the G. Natta Research Center in Ferrara, Italy.

Quantification of chain topology and microstructure in polyolefins challenges existing approaches. For example, changes in the long chain branch content as little as a few branches per hundred thousand carbon atoms can have a dramatic enhancement of the melt viscosity of polyolefins (3 branches per one hundred thousand carbons will triple the viscosity. [7,8] One current method for determination of long chain branch content involves measuring the number of trifunctional carbons using NMR despite the extreme dilution. Sensitivity to complex topological and micro-structural changes produced from the catalysts developed in this work will in some cases be more challenging than quantification of the extremely dilute long chain branch sites. Beaucage, in collaboration with researchers at LyondellBasell, have recently developed several analytic methods to address these issues including the use of neutron scattering data to quantify the topology and microstructure of complex polyolefins. In order to demonstrate these new methods we will first develop model microstructures through the use of anionic polymerization of polybutadiene followed by hydrogenation such as monodisperse star polymers, comb polymers, H-polymers and other controlled structures [9-12] in collaboration with Prof. Nifant'ev at the Moscow State University lab. We will then use these characterization methods to understand new polymers produced using commercially viable catalyst systems.

Advanced Polyolefins – commodity product, based on nano-assembled semi-crystalline materials: Commercial polyolefins based on ethylene and propylene homo- and copolymers are exceptionally versatile primarily because they are semi-crystalline solids with diverse, nano-sized crystallite morphologies, *Figure 1*. Since the invention of Ziegler-Natta catalysts, the polyolefin industry has developed many tools to control the size, shape, crystal structure, and interconnectivity of these crystallites via catalysis (e.g., with a controlled degree of stereo-regularization), polymerization conditions (with co-monomer selection and level, multi-reactor schemes, etc.), and processing conditions. The link between crystalline structure and chain microstructure has been qualitatively understood, however, it has only been in the recent few years that the link between crystalline structure, melting point and chain topology have been discerned using temperature rising elution fractionation and other methods. [13-15]

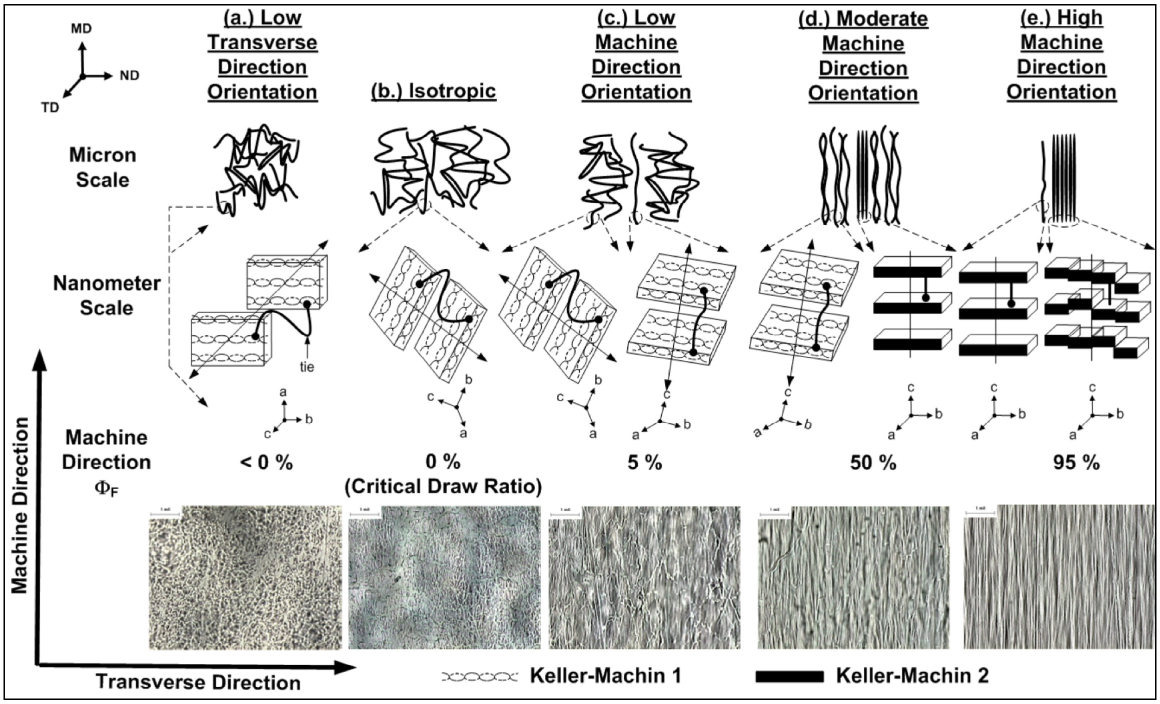


Figure 1. Schematic of crystalline structure changes on the micron and nanometer length scales during cold drawing. Nanostructural development is governed by chain chemical microstructure. Each of the sketches shows a low magnification (top) and high magnification (bottom) perspective. Included at the bottom of the figure are optical microscopic images collected in the various stages of the orientation process. [Taken from 16]

Traditional Polyolefin Catalysts – commercial Ziegler-Natta and single-site systems are sophisticated but approaching practical limits in product control: Recent decades witnessed enormous advances in two key areas. First, magnesium chloride-supported, multisite Ziegler-Natta catalysts with high activity were developed. [17-19] Advanced synthetic techniques and donor/modifier strategies effectively controlled the balance of active sites and catalyst stereoselectivity. Second, metallocene-based single-site catalysts provided high-performance polyolefins (polyethylenes, polypropylenes, polybutenes) with narrow molecular weight distribution (MWD) and unique microstructures. [20] Both catalyst types are structurally sophisticated and have been optimized for commercial use. However, each is approaching practical limits. *For instance, to what extent can the individual active sites of magnesium chloride-based Ziegler-Natta catalysts be further controlled through synthesis or use of donors and additives? What structural units can be incorporated in these polymers or those prepared using metallocenes?* Cost-effective ways to assemble advanced supramolecular structures based on inexpensive monomers, preferably with controlled placement of functional groups and branches, are needed.

1.2 Existing Research Environment in Professor Beaucage's Research Group and Complimentary Capabilities at LyondellBasell and at Moscow State University.

The proposed team provides a strong, multi-functional group that is up to the difficult task of developing new industrially viable approaches to control chemical microstructure in polyolefins.

Beaucage is best known for his work in small-angle scattering and in the development of scattering theory for complex disordered materials including macromolecules in dilute solution [21], equilibrium swollen networks [22,23], fractal aggregates [24] and nanomaterials. [25] Beaucage proposed and derived the Unified function for scattering which allows for the modeling of a wide range of hierarchical disordered materials using a single function. [26-27] Recently Beaucage has developed a method to quantify the topology of complex materials using small-angle scattering including short-chained branches [7], star polymers [28], long-chain branches [8], hyperbranched [29], cyclics [30], and biopolymers. [31] Beaucage's group is currently split between work on characterization of complex systems (2 graduate students), and work on synthesis of nanoparticles, heterogeneous catalysts and dye-sensitized solar cells (3 graduate students and 3 undergraduates including an NSF grant through CBET in the Engineering Division and support from USAID through the Higher Education for Development Program). Beaucage's facilities include preparatory labs for neutron scattering samples, static light scattering facilities, optical microscopes and extensive x-ray scattering facilities including two pinhole cameras on rotating anode sources and an ultra small angle scattering (Bonse-Hart) camera developed by Beaucage and a graduate student with funding from Procter & Gamble. Beaucage also has a synthesis lab.

Prof. Beaucage and Dr. Galiatsatos at LyondellBasell in Cincinnati offer unique capabilities in the characterization of the molecular and supra-molecular structures targeted by the proposed work. [7,8] Beaucage has developed a scaling approach using neutron scattering and small amounts of hydrogeneous polymers that can quantify details of the molecular topology and macromolecular, supramolecular and nano-structure of semi-crystalline polymers as a function of the catalyst structure and reaction conditions. The project will also use hybrid chromatographic fractionation techniques developed by Galiatsatos at the Cincinnati facilities of LyondellBasell to produce narrow molecular weight fractions of polymers from multiple catalytic sites in order to develop a fundamental understanding of the catalytic control over molecular structure.

Prof. Ilya Eduardovich Nifant'ev's extensive facilities at Moscow State University are centered on the development of catalysts for synthesis of polyolefins. Catalyst and chain transfer/shuttling development will be achieved by Prof. Nifant'ev in collaboration with Dr. Piemontesi, Dr. Nagy and through the application of high-throughput techniques, which is an area of expertise for Dr. Kristen. This team of experts provides a unique array of talents. Prof. Nifant'ev's group over the recent decade developed robust synthetic approaches toward a large variety of organometallic catalyst components resulting in more than 1000 isolated structures tested in polymerization systems, some of these were proven to have commercial implications. [32-34] Non-funded participants of the project will contribute to the success of the proposal: Dr. Piemontesi's lab at the G. Natta research center in Ferrara (Italy) is involved in developing new polyolefinic materials based on propylene and butene monomers [35]; Dr. Nagy is active in the areas of catalyst design utilizing computational techniques at LyondellBasell's Cincinnati Research Center [36]; Dr. Kristen directs the high throughput experimentation activities oriented toward polyolefin research at the Frankfurt research center of LyondellBasell. [37]

This Proposal Represents a New Research Direction

The proposed research represents a new research direction for Prof. Beaucage and Prof. Nifant'ev since the use of chain transfer agents to produce new chain microstructure and topologies has not been previously considered by either of the PI's or LyondellBasell. The project also involves production of monodisperse, model-branched structures for verification of new characterization techniques which is a research direction not currently funded or being investigated by the PI's or by LyondellBasell. Current work supported by LyondellBasell focuses on existing commercial resins and commercial catalyst systems using traditional approaches.

Most Important Initial Results

1) Development of model to quantify chain microstructure using small-angle neutron scattering. [38]
2) Development of method for quantification of local structural features using neutron scattering. [7,8,38,28-31]
3) Development of capabilities for TREF and other fractionation techniques for separation of complex mixtures of variable chain topology at LyondellBasell in Cincinnati. [13-15]

4) Expertise and track record of Prof. Nifant'ev in the development of catalyst structures tested in polymerization systems, some of which had commercial value. [32-34]
5) Demonstration of high throughput catalyst testing at Frankfurt facilities of LyondellBasell. [37]
6) Development of modeling and industrial production capabilities of LyondellBasell in Cincinnati and in Ferrara, Italy. [36]

Important Issues to Address:

A number of scientific and technical issues will be addressed in the proposed research:

1) Development of new approaches towards advanced polyolefinic materials using nonconventional polymerization methodologies based on a combination of living polymerization catalysts and customized chain control agents.
2) Development of controllable supramolecular architecture based on targeted placement of polyolefin and functionalized polyolefin blocks. While we can build on recent advances in controlled chain transfer techniques in coordination polymerization systems [39,40], further progress is required in improving the control over the complex chemical systems, developing methods to introduce polar functions in a controllable fashion and establish reliable structure characterization techniques that can quantify supramolecular and molecular topology.
3) Development of improved single-site transition metal catalysts with high activity and very low contribution of chain transfer processes (preferably living polymerization in commercially viable elevated temperatures). We'll utilize rational catalyst development techniques guided by computational insight.
4) Development of new, more efficient and customized, reversible chain transfer agents, capable of carrying various functional groups. This field requires development of conceptually new systems and cost-efficient ways of preparing these agents.
5) Establishing new polymer characterization techniques for reliable structure assignment for the new materials and enabling understanding of the complex relationship between supramolecular and molecular topology and catalysis, as well as novel characterization techniques for these designed materials and their self-assemblies in solution and in the solid state.

1.3 Objectives

The new polymers are expected to have controllable supramolecular architecture, based on targeted placement of polyolefin and functionalized polyolefin blocks. While we can build on recent advances in controlled chain transfer techniques in coordination polymerization systems [39,40], further progress is required in improving the control over the complex chemical systems, developing methods to introduce polar functions in a controllable fashion and establish reliable structure characterization techniques that can quantify supramolecular and molecular topology.

The key focus areas in achieving a significant step forward in this challenging problem are:

1) Development of improved single-site transition metal catalysts with high activity and very low contribution of chain transfer processes (preferably living polymerization in commercially viable elevated temperatures). We'll utilize rational catalyst development techniques guided by computational insight.
2) New, more efficient and customized, reversible chain transfer agents, capable of carrying various functional groups. This field requires development of conceptually new systems and cost-efficient ways of preparing these agents.
3) Establishing new polymer characterization techniques for reliable structure assignment for the new materials and enabling understanding of the complex relationship between supramolecular and molecular topology and catalysis.

1.4 Proposed Work

The project will have three main tasks:

Task 1) Catalyst development for controlled microstructure polyolefins, *Figure 2*.

Task 2) Development of model branched structures and blends for verification of the characterization techniques used for catalyst development.

Task 3) Development of new polymer characterization techniques to enable quantification of chemical microstructure and topology.

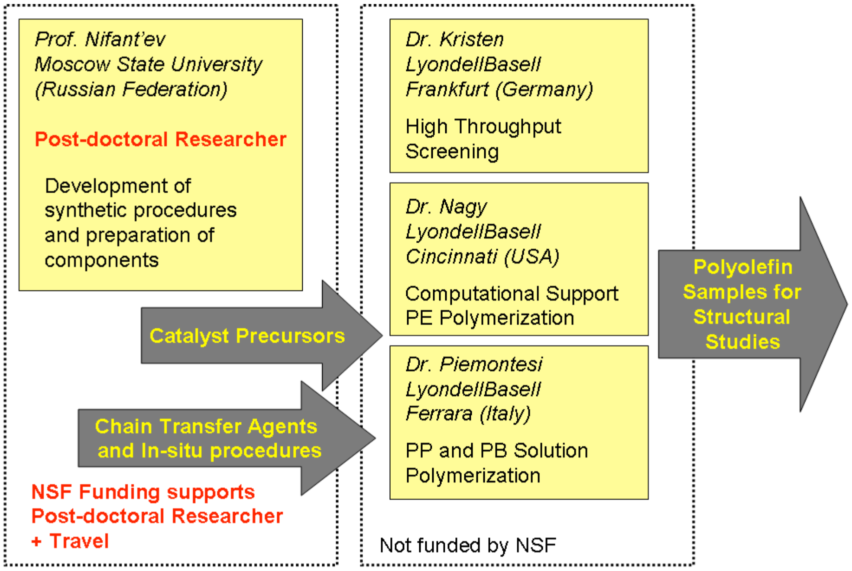


Figure 2. Schematic of interaction in Task 1.

1.4.1 a Next Generation Catalyst Systems - Shaping the Future of Polyolefins.

Within the last decade, mixed single-site catalysts have been used to generate controlled multimodal resins (Scheme 1, *Figure 3a*) or highly branched polymers using a single or multi-monomer feedstock (Scheme 2, *Figure 3b*). After intensive research, several systems achieved commercial status for making polyethylene grades with improved performance.

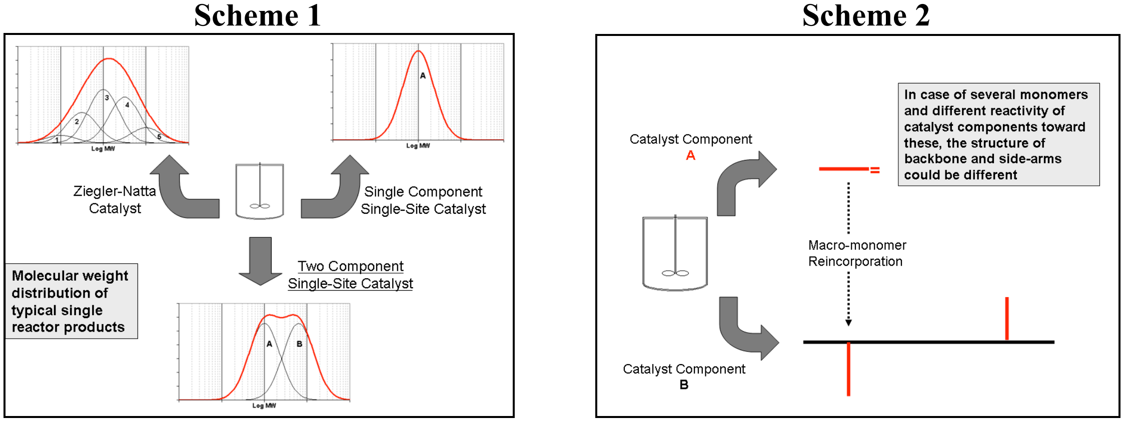


Figure 3. a) Scheme 1 single-site catalysts for controlled multi-modal resins. b) Scheme 2 single site catalysts for highly branched polymers.

Recent advances in coordinative polymerization include controlled chain-transfer techniques that potentially allow manufacturers to expand the range of accessible polyolefin architectures are shown in Schemes 3 and 4, *Figure 4*. [39,40]

Post-metallocene single-site catalysts that provide varying degrees of comonomer incorporation efficiency and chain-transfer/chain-termination properties enabled these new polymer synthesis strategies. Scheme 5, *Figure 5*, illustrates frequently reported precursor complexes. [40]

Expansion of Post-Metallocene Diversity – enabling factor in new polymer and process design

Interest in the chemistry of catalyst precursors is gradually shifting from metallocenes to post-metallocenes, and many of the newly published precursors incorporate chelating ligands. Diverse ligand environments and vast experimentally "uncharted territories" promise a vibrant future for the development of enhanced polyolefins at reduced manufacturing costs. Advanced computational tools and high-throughput experimentation are essential for efficient research and development in this area. An integrated catalyst-process-product design strategy demands convenient, inexpensive synthetic strategies for ligand candidates starting from easily accessible precursors.

Scheme 3 **Scheme 4**

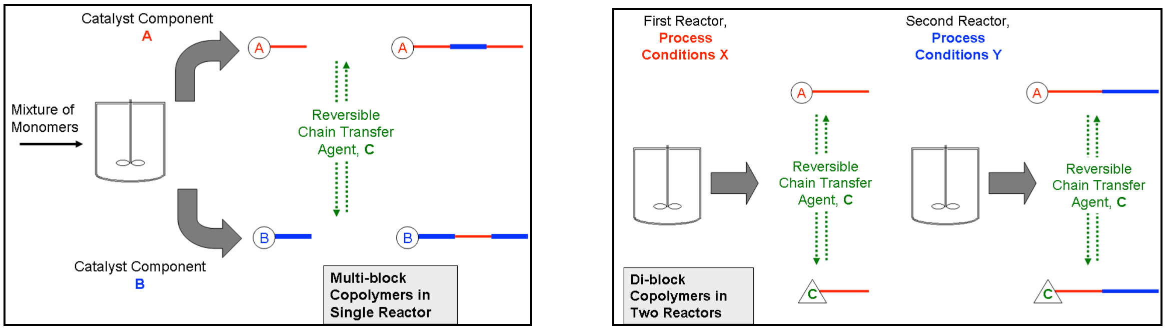


Figure 4. a) Scheme 3, multi-block copolymers using chain transfer agents. b) Scheme 4, di-block copolymers using two reactors and chain transfer agents.

Scheme 5

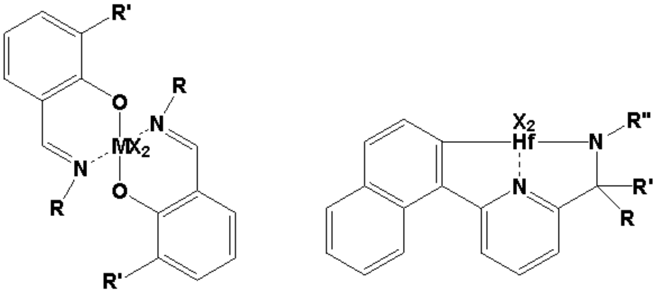


Figure 5. Frequently reported precursor complexes for post-metallocene single-site catalysts. [40]

Our recent studies indicate that the quinoline moiety is a particularly versatile template that supports diverse ligand topologies. We successfully developed a flexible synthetic approach to prepare quinoline compounds strategically functionalized in the 2- and 8-positions. We also identified selective metallation procedures that give new classes of promising catalyst precursors (Scheme 6, *Figure 6*).

Scheme 6

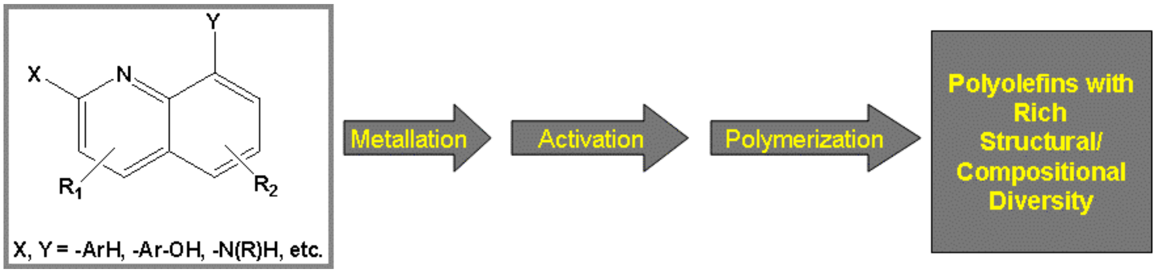


Figure 6. Scheme 6, use of quinoline as a precursor to a new class of post-metallocene catalysts.

Activated and tested under commercially relevant conditions, the new catalysts demonstrate good stability and high activity in ethylene and propylene (co)polymerizations. Preliminary analysis of the polyolefins indicates a dramatic effect of ligand environment and activation procedure on the polymer structure and composition. Remarkably, the new polymers are structurally and compositionally diverse. This is likely due to the multi-site nature of the catalysts; site diversification might occur during catalyst formulation as well as during polymerization. We believe that this generation of "non-spectator" ligands can be used to design new polymerization technologies. *The interplay of the active sites and their influence on polymer architecture is not yet known and will constitute one of the research areas of our proposal.*

Nontraditional Chain-Transfer Agents – a new research direction in coordination catalysis

As a key program element, we propose to expand the list of agents now used in reversible chain-transfer scenarios (Schemes 3 and 4, *Figure 4*) beyond dialkylzincs or trialkylaluminums. In addition to identifying more efficient systems, we will explore several ways to use the chain-transfer agent as a "vehicle" to introduce reactive functionalities into the polyolefin. This aspect will require commercially viable, robust synthetic approaches to the new reagents.

1.4.1 b Key Deliverables/Milestones - Catalyst Component and Polymer Synthesis

First year:

Catalyst complexes: Prepare benchmark complexes and diverse representatives of the quinoline-based precursor family of Scheme 6, *Figure 6*.

Chain-transfer agents: Evaluate synthetic approaches to prepare new zinc alkyl compounds.

Computational chemistry: Develop computational descriptors for chain-transfer processes.

High-throughput technique: Develop a robust solution polymerization testing procedure using literature benchmarks.

Second year:

Catalyst complexes: Continue to diversify quinoline-based precursors.

Chain-transfer agents: Develop a commercially viable in-situ approach to generate new chain-transfer agents.

High-throughput technique: Broadly screen combinations of precursor complexes and chain-transfer agents.

Medium-scale lab polymerization: Prepare large (~100 g) polyolefin samples using new catalyst precursors and traditional chain-transfer agents.

Third year:

Chain-transfer agents: Optimize a commercially viable in-situ approach to the most promising chain-transfer agents.

High-throughput technique: Investigate process conditions with a selected precursor/chain-transfer agent combination.

Medium-scale lab polymerization: Prepare large (~100 g) polyolefin samples using new catalyst precursors and newly developed chain-transfer agents.

1.4.2 a New Quantification of Chain Microstructure and Topology, and Synthesis of Model Chain Topologies for Development of Characterization Methods.

Branched & Network Polymers: The control & understanding of chain microstructure and branch content has been an active area of research for polymer scientists for several decades. Branching strongly affects the dynamic properties of polymers due to the formation of quiescent networks. Long chain branching has the strongest effect on rheological properties, yet has been particularly difficult to quantify since the number of branch sites is often small, as determined by NMR for instance. Alternatives to colligative techniques such as NMR have failed to provide quantitative measures of long-chain branching due to the complexity of the non-linear dynamic response of branched structures associated with a hierarchical chain structure. This proposal will implement a new analytic approach that enables structure/property control in branched systems. [38] This new characterization method will be used in the development of new catalysts and polymer microstructure.

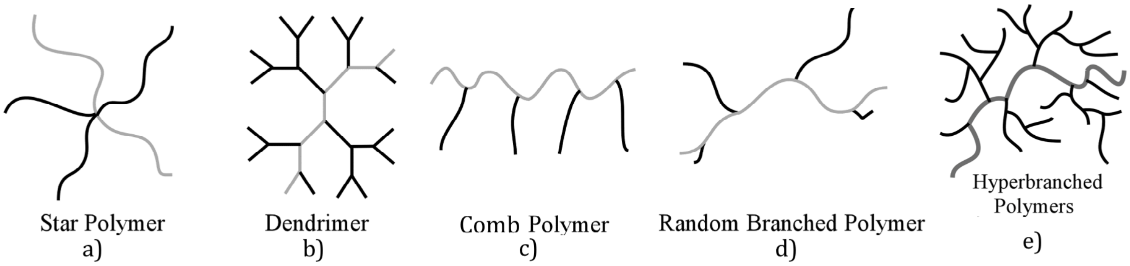

Star Polymer a)
Dendrimer b)
Comb Polymer c)
Random Branched Polymer d)
Hyperbranched Polymers e)

Figure 7. Different branched structures as discussed in text; bold-grey indicates a minimum path through the structure of length p.

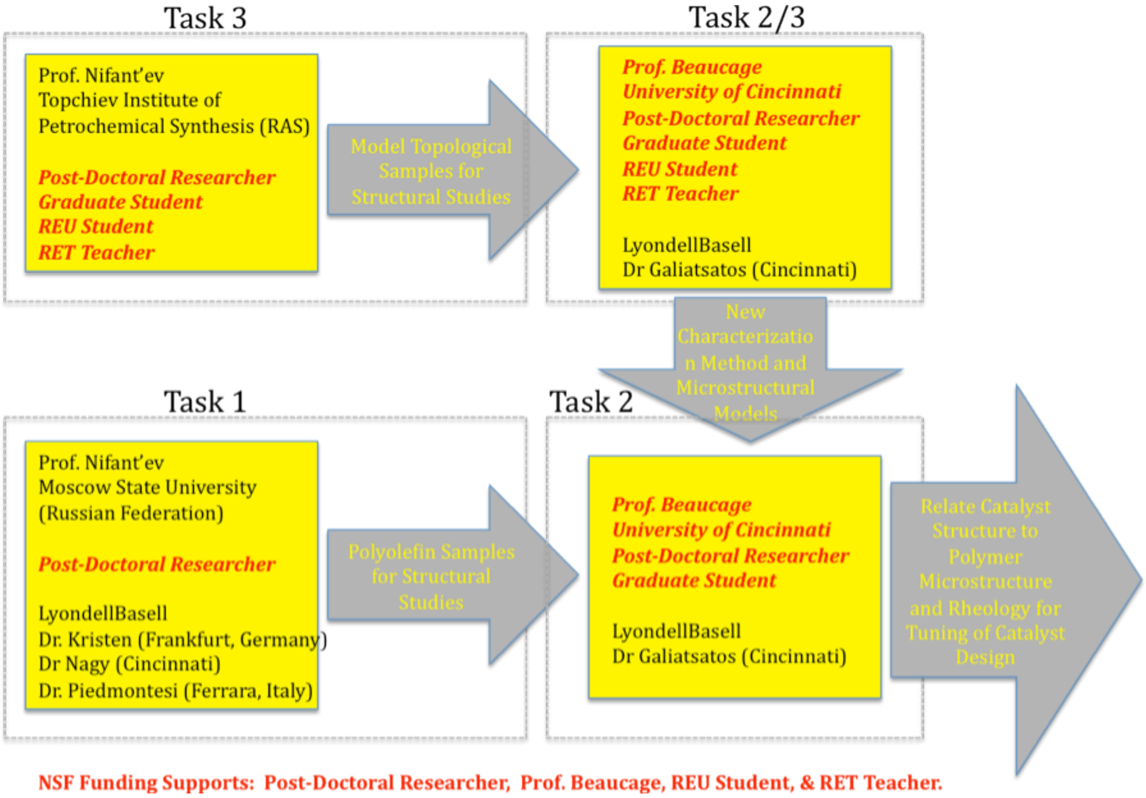
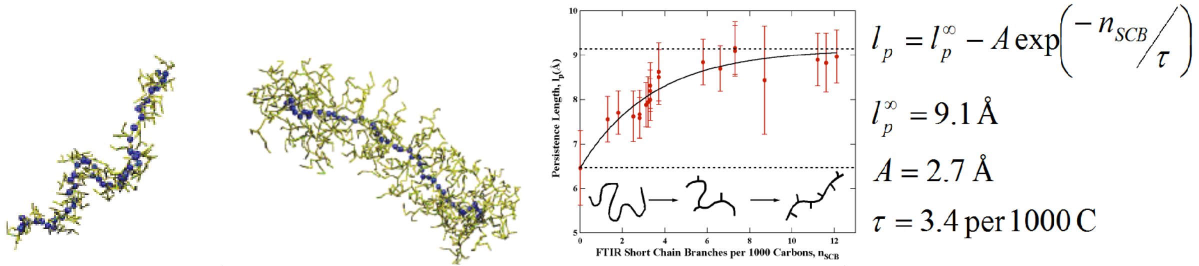


Figure 8. Schematic of interactions in Tasks 1 to 3.

Branches in macromolecules can be classified in terms of short (SCB) or long (LCB) chain branching where a long branch is one that is indistinguishable from the main chain. [41-44] SCB's primarily affect local structure such as the persistence length. [7,45] SCB's affect crystallinity and miscibility.



a) b)

Figure 9. a) Monte Carlo simulation results of short chain branching by Connolly et al.. [45] b) Variation in Persistence length, as measured by small angle neutron scattering, with short chain branch content for polyethylene. [7]

When branches become indistinguishable from the main polymer chain, branching does not significantly affect persistence since the number of branch sites is few, but branching has a large effect on chain scaling and rheology. [46,47]

Quantification of Branching in Polymers: Table 1 compares existing techniques to quantify branching in macromolecules. Relative measures of branching obtained from GPC and rheological measurements are routinely used for estimating branching in polymers. NMR has also been employed for determining branch content in polymers by detecting the frequency shifts for carbon atoms at branch points using high-frequency ^{13}C-NMR for PE and PVC. The viability of these techniques to estimate branching and topology from existing literature and the shortcomings are summarized in Table 1 with a list of references. All of these techniques will be part of the characterization performed at LyondellBasell's Cincinnati Technical Center in collaboration with Beaucage. Scattering will be performed at national user facilities.

Table 1. Comparison of Characterization Techniques.

	Technique	Effective in measuring		Nature	What they measure	References
		LCB	SCB			
1	GPC	Yes	No	Relative	Qualitative	[48-53]
2	NMR	No	Yes	Absolute	$<n_{br}>$ for PE and PVC	[53-61]
3	Rheology	Yes	No	Relative	Qualitative	[62-87]
4	Scattering	Yes		Absolute	Absolute ϕ_{br}, c, d_f, l_p, $\boldsymbol{n_i}$, $<n_{br}>$, $<z_{br}>$	[21,24-31,38,47,57,88-94]

LCB/SCB: long/short chain branching, n_{br}: number of branch points, z_{br}: length of branches, ϕ_{br}: mole fraction of material in branches, c: connectivity dimension, d_f: fractal dimension, l_p: persistence length, n_i: inner fraction, PE: polyethylene, PVC: polyvinylchloride.

Our Recent Work On Quantification of Branch Content in Randomly Branched Polyethylene by Small Angle Scattering: [38]

Beaucage [38] has given a new approach to quantify branch content by considering the scattering contributions from chain-like aggregates. Such a description has been applied to polymer chains [8,38,88], ceramic aggregates [38,95] and biomolecules. [31] An aggregate structure can be linear or branched, as shown in *Figures 7 & 10*. [38] The open circles, connected in a chain of p primary units, in *Figure 10b*, represent the minimum path through the structure. A scaling relationship between the degree of polymerization, z, the number of units in the minimum path, p, and the overall coil/aggregate size R_2 and the size of the Kuhn step R_1 [38,96,97] can be given as,

$$p^c = z = (R_2/R_1)^{d_f} \tag{1}$$

where c in eqn. (1) is known as the connectivity dimension, which is equal to 1 for a linear chain, and increases with more complex microstructure. d_f is the mass fractal dimension. A second scaling relationship between the above terms could be expressed with the minimum dimension d_{min} [96,97] where d_{min} represents the mass fractal dimension of the minimum path (*Figures 7 and 10*) or the tortuosity of the chain path in the absence of branches.

$$p = \left(R_2/R_1\right)^{d_{\min}} \qquad \text{where} \qquad d_{\min} = d_f/c \tag{2}$$

Beaucage [38] showed that one could obtain branch content from eq. (1) and eq. (2) as follows,

$$\phi_{br} = \frac{z-p}{p} = 1 - z^{\frac{1}{c}-1} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{\min}-d_f} \tag{3}$$

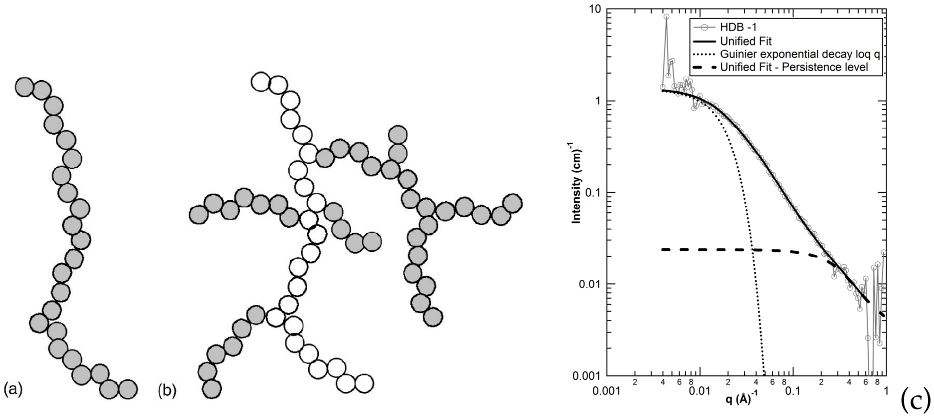


Figure 10. a) Linear aggregate, b) Branched aggregate; composed of primary particles. The open circles in b) represent the minimum path, p, through an aggregate. [38] c) Neutron scattering data from 1 % hydrogeneous branched polyethylene in deuterated p-xylene at 125 ºC fit to the Unified Equation. [7] The dashed line at high-q is scattering due to the persistence unit, low-q dashed line is Guinier's law for the coil.

The scattering pattern, *Figure 10c*, displays the persistence regime at highest-q indicated by the dashed curve from which the persistence length is measured. At lower q the coil regime is composed of a Guinier curve [26,92,98], fine dashed curve,

$$I(q) = G\exp\left(-q^2R_g^2/3\right) \tag{4}$$

where G is a constant and R_g is the radius of gyration, and a power-law decay [26,92],

$$I(q) = B_f q^{-d_f} \tag{5}$$

where B_f is a constant and d_f is the mass fractal dimension. The parameter d_{min} can be calculated from scattering using eqns. (4) and (5) to account for branched structures [38],

$$d_{\min} = B_f R_{g2}^{d_f} \Big/ \left(C_p G_2 \Gamma\left(d_f/2\right)\right) \tag{6}$$

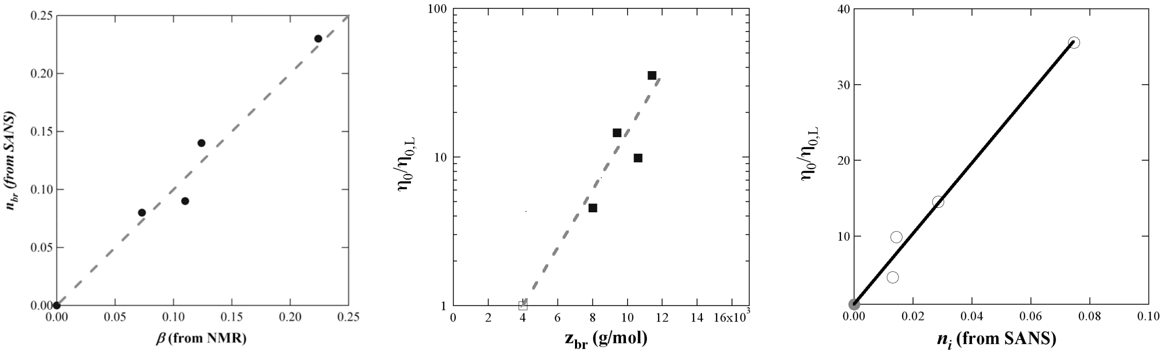
where G_2 is the Guinier prefactor (eq. (4)) for the aggregate, R_{g2} is the aggregate radius of gyration (eq. (4)), d_f is the mass fractal dimension (eq. (5)) and B_f is the power-law prefactor (eq. (5)). C_p is a scattering polydispersity factor described by Sorensen [7,99] and given by,

$$C_p = \left(z_1/z_2\right)\left(z_{2+2/d_{f2}}/z_2\right)^{d_{f2}/2} \tag{7}$$

where z_i is the i'th moment of the degree of polymerization, z. $C_p = M_z/M_w$ for $d_{f2} = 2$. Details of these data fits are described in a recent paper. [7]

Ref. [7] describes how a wide range of microstructural parameters can be directly calculated from SANS data using this scaling analysis. For example, *Figure 11a* shows the number of branches per chain, n_{Br}, calculated with no free parameters directly from SANS, compared with the same value obtained from NMR. NMR cannot determine the average length of a branch, z_{Br}, which is shown from SANS in *Figure 11b*. The average branch length, z_{br}, can have significant impact in understanding the rheological behavior of long chain branched polymers. *Figure 11b* shows a log-linear plot of the zero shear viscosity enhancement, $\eta_0/\eta_{0,L}$, as reported by Costeux et al. [100], versus the average branch length, z_{br}, from SANS. An exponential increase in $\eta_0/\eta_{0,L}$ with increasing branch length is observed. Extrapolation of the line in *Figure 11b* intercepts the z_{br} axis around 4000 g/mole. This implies that the viscosity enhancement effect due to long chain branching starts to occur, when the average branch length (weight average) becomes about three times the entanglement molecular weight, M_e, of 1250 g/mole. It has been previously reported that for a branch in a polymer like polyethylene to have a significant effect on the rheological properties, branches need to be at least twice M_e (number average). [101]

Based on previous studies, the viscosity enhancement can also be attributed to the average number of inner segments per chain, n_i, as described in ref. [8], in branch-on-branch polymer chains. Inner segments are chain segments ending in two branch points and exist in branch-on-branch or hyperbranched structures. *Figure 11c* shows a plot of viscosity enhancement, $\eta_0/\eta_{0,L}$, versus n_i obtained directly from SANS with no free parameters. The plot shows a linear increase of viscosity enhancement with increasing number of inner segments for the samples studied. A linear fit to the values obtained from SANS intercepts at no viscosity enhancement ($\eta_0/\eta_{0,L} = 1$), grey circle. This supports the proposition that inner segments are highly important to the enhancement of viscosity in systems displaying branch on branch structure.



(a) (b) (c)

Figure 11. (a) Plot of number of branch sites per chain, n_{br}, calculated from SANS against average number of branches per chain, β, from NMR. [100] (b) Log-linear plot of zero shear viscosity enhancement for linear polyethylene of same M_w [8] against average length of branch, z_{br} from SANS for weakly branched HDB samples. (c) Linear plot of zero shear viscosity enhancement [8] against number of inner segments per chain, n_i from SANS, for the HDB samples.

Specific Controlled Branching Samples to be Studied and Expected Behavior:

Symmetric Star Polymers: Star polymers are polymers with a single junction point and f arms. Since two of the arms will form a minimum path through the structure (*Figure 7a*) the mole fraction branching is simply $\phi_{br} = (f-2)/f$. The minimum path is given by $p = 2\ z/f$, which leads to a connectivity dimension of $c = \ln(z)/(\ln(z)+\ln(2/f))$. The average branch length for a star is $z_{br} = z/f$. The number of branches for a star is $n_{br} = f-2$. Symmetric polybutadiene and hydrogenated polybutadiene star polymers with f = 3, 6, 9 and some higher functionalities will be synthesized. [9] A series of asymmetric star polymers that parallel the symmetric star polymers in molecular weights will also be synthesized. Variability in z_{Br} with asymmetry of the star architecture is of interest. n_{Br} should remain constant for these matched symmetric/asymmetric polymers.

Comb Polymers: For evenly spaced comb polymers with significant branch length, $n_i = n_{br} - 1$ inner segments. Also, $\phi_{br} = n_{br}/(2n_{br} + 1)$ and $z_{br} = z/(2n_{br} + 1)$. For other comb architectures similar relationships can be obtained. A number of comb and branch-on-branch modified comb polymers will be synthesized. [85]

Model Short Chain Branched Polyolefins: If the branch length is sufficiently small compared to the main chain and if a significant number of short branches occur on a comb polymer, we expect to see enhancement of the persistence length rather than scaling effects. [7] A series of poly(ethylene-co-1-butene) copolymers will be synthesized to study this effect. [11] Variable branch length is also of interest. Additional commercial samples of this type are also available with variable content of hexane comonomer from 0.25% to 5 % and with molecular weights on the order of 100 kg/mole and polydispersity indices of about 2.

H-Polymers (a-w Type Polymers or Pom-pom Polymers): H-polymers display a unique value for n_i that can be a useful test of our ability to measure inner fraction. A series of H-polymer and pom-pom polybutadiene and hydrogenated polybutadiene polymers will be produced. [9,12]

Blends of Branched Polymers of Variable Architecture and Linear Polymers: Commercial long chain branched polymers are typically blends of 3 arm star polymers and linear polymers with some branch on branch structure. It is important to verify the sensitivity of the proposed analytic method using blends of monodisperse polymers of variable functionality.

Quantification of Polydispersity in Branched Structures: Following the work of Sorensen [7,99] the polydispersity of a branched polymer blend can be quantified through the parameter C_p as mentioned in equations (13) and (14). Verification of this approach can only be made by blending controlled molecular weight and branched polymers of the types discussed above.

1.4.2 b Key Deliverables/Milestones – Model Polymers with Controlled Microstructure and SANS Method.

Proposed Work Using Model Chains and Development of SANS Method, Tasks 2/3:

1) Anionic synthesis of controlled topology polymers at the Moscow State University under the direction of Prof. Nifant'ev and involving the graduate student, REU undergraduate student and the post doctoral researcher. The RET high school teacher will also be involved in this work.

2) Transfer of the anionic synthetic techniques involving synthesis of polybutadiene followed by hydrogenation for linear, comb, star, and other more complex topologies to Cincinnati.

3) Experimental determination of branching topology on model samples and blends using SANS at US user facilities in Oak Ridge and at NIST and other techniques available in our lab such as dynamic light scattering and at LyondellBasell's facility in Cincinnati.

4) Measurement of melt rheology for correlation with SANS and synthetic topology.

5) Development of models that will be used to measure and predict properties of branched polymeric systems based on the structural model from SANS measurements.

Tasks 2/3: Development of model chain topologies of low polydispersity and SANS Method.

First year:

The post doctoral researcher will reside in Moscow at MSU. He will setup arrangements at the Moscow State University for the anionic polymerizations using facilities that already exist. The graduate student will join the post-doc after about 6 months to begin work on the model polymer synthesis. The REU undergraduate will join the graduate student and post-doc in the summer. Both the undergraduate and graduate students will spend about 10 weeks in Moscow working on the synthesis of model structures. Monodisperse, linear polybutadiene chains will first be synthesized, followed by symmetric star polymers. Initial neutron scattering measurements and characterizations at Lyondell's Cincinnati facility will begin in the first year.

Interaction with Task 1: Initial controlled topology samples will be available at the end of the first year. These will be included in neutron scattering measurements and will be characterized using dynamic light scattering and rheology at UC and in the characterization facilities of LyondellBasell in Cincinnati.

Second year:

Synthesis of comb polymers. Continuing neutron scattering measurements and other analytic work will proceed. Shorter visits by the graduate student and REU undergraduate to Moscow will be necessary. Setup synthesis capability in Cincinnati for anionic polymerization.

Interaction with Task 1: Feedback between polymer characterization and catalyst development. Characterization of commercial viability studies for catalyst-transfer agents. Use some of the SANS results to guide the high-throughput technique. Examine medium scale synthesis samples for feedback with the catalyst work and comparison of lab scale with scaleup.

Third year:

Model short chain branched and H-polymers will be synthesized. Continued refinement of the SANS analysis and measurements.

Interaction with Task 1: Detailed microstructural analysis of optimized commercially viable in-situ approach for the most promising chain-transfer agents. Consider some of the cases for the high-throughput process study to tune the high-throughput study guidelines. Characterize results of moderate scale synthesis of target catalysts.

2. BROADER IMPACT OF THE PROPOSED WORK

2.1 Benefits to Society and Industry

The proposed work will contribute to the development of improved polymers for commercial application as well as improving our understanding of the relationship between chain microstructure and physical properties. This understanding will be of use with a wide range of macromolecular materials including renewable plastics as well as biomaterials such as proteins as demonstrate by Beaucage. [31] The scattering approach is also applicable to understanding growth mechanisms and properties of branched disordered ceramic aggregates. [95] The understanding developed in this work is therefore applicable to a broad range of problems of importance to chemists.

2.2 Education and Knowledge Dissemination

The project is designed to expose young scientists to the international research community as well as to develop ties between science in the Russian Federation and the US. Non-funded participation of researchers at labs in Frankfurt, Germany and at the G. Natta Research Center in Ferrara, Italy will further expose young researchers to a broad range of international research. This includes a post-doctoral researcher, a graduate student and an undergraduate student. The project will also include participation of a high school teacher who will spend one month per year in Moscow working on anionic polymerization as well as participating in the School of Education at Moscow State University. This exposure will broaden the scientific experience of the teacher as well as the students with whom he/she interacts in the US, encouraging further international exposure. These interactions will broaden scientific interactions with Russia as well as developing a diverse, globally-engaged, US science and engineering workforce. The project will select where possible minority and women participants for the participating students and teacher. The PI has a track record of engaging minorities and women in similar REU and RET projects. The undergraduate, graduate students and the post-doctoral researcher will also be exposed to the research environment at US national labs in performing neutron scattering measurements at Oak Ridge and NIST.

New web based course on novel polyolefin materials will be added to the PI's web suit of courses that averages over 70 independent hits per day with over 260,000 independent IP hits since 2000. The course will cover catalytic chemistry of controlled microstructure, analytic characterization of microstructure and industrial processes used for production of polyolefins. The post-doctoral student will be involve in preparation of this course and will teach some of the lectures from Moscow. Lectures by Prof. Beaucage and Prof. Nifant'ev will be linked through the use of an Internet based classroom available at both universities.

3. MANAGEMENT PLAN

The project will chiefly involve two sites, Moscow State University and the University of Cincinnati. Both sites have access to web based conferencing facilities so a weekly meeting lasting about one hour is possible to maintain contact between the groups and to plan interactions and sample transfer. Of particular importance is the mentoring of both the post-doctoral student and the graduate student during their time in Moscow. Beaucage will be in frequent e-mail contact with the students and post-doc. In addition to the weekly web meetings Beaucage will travel to Moscow once a year and will spend a more extended time in Moscow the first year to help setup the project with the post-doc. Beaucage has not traveled to Moscow previously, however, the LyondellBasell participants have had contact with Prof. Nifant'ev and his group at Moscow State University for a number of years, so there are existing strong contacts through the industrial partners. Prof. Nifant'ev also plans to travel to Cincinnati, Frankfurt and Ferrara during the project using support from the Russian Foundation for Basic Research (RFBR). RFBR will also supply funds for materials used in Moscow at the Moscow State University where model polymers will be synthesized. In Moscow, Prof. Nifant'ev will be in charge of day-to-day management of the post-doctoral researcher and visiting graduate student and undergraduate student.

4. RESULTS FROM PREVIOUS/CURRENT NSF AWARDS

The PI is currently supported on a one year no cost extension by NSF award 0626063 from CBET, *Spray Jet Flames for Supported Gold Catalysts: New Catalysts by Design.* 09/01/06 to 08/31/10. The project has supported a US resident PhD student, a minority high school teacher (2 summers) and 4 female and one minority undergraduate student. The graduate student and one of the REU undergraduates spent more than 6 months in Zurich Switzerland as part of this project. A spray flame reactor was developed for the production of supported gold catalysts on metal oxide supports for room temperature oxidation of CO. Nano-scale gold catalysts were produced on titania, silica, alumina and iron oxide supports. The mechanism of formation of these supported catalysts was studied in the flame using in situ anomalous x-ray scattering (ASAXS) at the Advanced Photon Source of Argonne National Laboratory as well as at the NSF funded CAMD synchrotron facility at LSU. The reactivity of the supported catalysts was studied using a quartz reactor coupled with a mass spectrometer for monitoring the exhaust gasses. For comparison, Au/TiO_2 catalyst was also synthesized using deposition precipitation (DP) method. For the CO oxidation reaction, it was observed that the activity of catalyst prepared by deposition precipitation DP method is higher then those prepared by spray flame pyrolysis (SFP) for the same weight loading of gold. SFP has the advantage that it is a continuous process and can produce these supported catalysts at a much higher rate and at a lower cost. While the SFP gold particles are larger and have a broader size distribution, the lower activity of SFP catalysts seems to be primarily associated with the shape of the particles that differ between the two preparation methods. Gold particles from the DP method seem to be two-dimensional with a height of less than two atomic-layers. In contrast, the SFP gold particles are three-dimensional nano-crystals embedded on the TiO_2 surface. There are also differences in the morphology of the titania support phase between pyrolytically formed catalysts and those produced by DP using commercial TiO_2. The effects of catalyst support structure in the DP method were studied using TiO_2 produced in SFP of variable morphology. The activity of catalysts prepared using the flame made TiO_2 is even higher then the catalysts made using commercial TiO_2. The work involved extensive use of EXAFS facilities at ESRF in Grenoble, France. The project has also involved independent projects by REU, RET, IREE students and scientists involving other nanoparticulate aerosols such as carbon soot from diesel engines, iron oxide nanoparticles, carbon-coated titania and platinum catalysts supported on alumina. Two papers are in submission associated with this work and four papers are being prepared. Prior publications associated with the preparation of catalysts by the co-PI (out of 115 peer reviewed papers) include a paper in *Nature Materials* **3** 370-374 (2004) by Beaucage G, Kammler HK, Mueller R, Strobel R, Agashe N, Pratsinis SE, Narayanan T as well as 6 further papers listed below:

1) Kammler HK, Beaucage G, Kohls DJ, Agashe N, Ilavsky J *J. Appl. Phys.* **97** 054309 (2005).
2) Beaucage G *Phys. Rev. E* **70** 031401 (2004).
3) Mueller R, Kammler HK, Pratsinis SE, Vital A, Beaucage G, Burtscher P Powd. Tech. 140 40-48 (2004).
4) Kammler HK, Beaucage G, Mueller R, Pratsinis SE *Langmuir* **20** 1915-1921 (2004).
5) Kammler HK, Jossen R, Morrison PW, Pratsinis SE, Beaucage G *Powd. Tech.* **135** 310-320 (2003).
6) Hyeon-Lee J, Beaucage G, Pratsinis SE *Langmuir* **14** 5751-5756 (1998).

5. SUMMARY OF THE PROPOSED INTERACTION WITH MOSCOW STATE UNIVERSITY AND LYONDELLBASELL

5.1 Visits Between the US Researchers and Students and Their Partners Abroad

The proposed work will involve trips by Beaucage and his graduate student, undergraduate REU students and a RET (research experience for teacher) participant to MSU to visit the laboratory of Prof. Nifant'ev as well as visiting the German, Italian and Cincinnati Laboratories of LyondellBasell. Several short visits are planned on an annual basis while the graduate student and undergraduate REU students will spend 10 weeks learning catalytic techniques that can be transferred to the Cincinnati Lab of Beaucage. Similarly, the post-doctoral student and Prof. Nifant'ev will visit Cincinnati and the US labs of LyondellBasell (also in Cincinnati). In the first year Beaucage will spend about one month in Moscow setting up the project and performing other project activities.

<u>The collaborative approach to be used and the expected synergy</u>: Catalyst systems developed and synthesized in Moscow will be used to prepare new polyolefinic materials and distributed to the non-funded participants in Ferrara, Frankfurt and Cincinnati. Samples will be delivered to Cincinnati for characterization using TREF and scattering techniques in the laboratory of Beaucage as well as at national user facilities at ORNL and NIST. Results of this characterization will be discussed in weekly web-based videoconferences. Annually, the Cincinnati participants will travel to Moscow and to the European labs of LyondellBasell for discussions of the results. The graduate and undergraduate students will spend approximately 10 weeks per year in the labs of Prof. Nifant'ev in Moscow studying catalysis. The post-doc will visit the labs of Beaucage and the facilities of LyondellBasell in Cincinnati to learn the novel characterization techniques. All of the US participants will attend Russian existing language programs in the college of Chemistry at MSU.

5.2 Anticipated Scientific Benefits of the Interaction.

Prof. Ilya Nifant'ev is an expert in organic and organometallic synthesis and he will lead the development of new catalysts and chain transfer agents. The post-doc will primarily work with Prof. Nifant'ev in Moscow. The collaboration also offers unfunded participation by four research scientists at LyondellBasell Corporation who will offer expertise in industrial catalyst development, high-throughput polymerization techniques and polyolefin characterization. Coupled with the PI's expertise in polyolefin characterization and development of novel analytic methods using neutron scattering the team is ideally suited to address the development of novel polyolefin architectures using advanced catalysis and group transfer agents. The proposed work will develop a new interaction between Moscow State University and the University of Cincinnati.

The main scientific benefits of the proposed interaction between UC and MSU are:

1) Expertise in the development of novel catalysts, and chain transfer agents.
2) Expertise and access to facilities specializing anionic polymerization of polybutadiene at the Moscow State University.
3) Complementary expertise in characterization of chain microstructure and topology at Cincinnati.
4) Joint interactions with LyondellBasell with associated complementary expertise in olefin polymerization, high-throughput synthetic methods, and polymer characterization.
5) Strong interest by all participating scientists in the project as it directly relates to their main scientific interests.

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1980 University of Rhode Island, Kingston, RI 02881 ***B.S. Zoology***; Highest Distinction. (National Merit Scholar Finalist, Elected to Phi Beta Kappa)

1982 University of Rhode Island, Kingston, RI 02881 ***B.S. Chemical Engineering;*** High Distinction. (Elected to Phi Kappa Phi)

1991 University of Massachusetts, Amherst, MA 01003 ***Ph.D. Polymer Science and Engineering***. Advisor: ***Richard S. Stein***. *A Morphological, Mechanical and Thermodynamic Investigation of the Isotactic-PVME/PS Polymer Blend.*

1991 Sandia National Laboratory, Albuquerque, NM 87185; ***Post Doctoral Fellow***, Organic Materials Group *Characterization of nanomaterials using scattering & scattering theory.*

Appointments

University of Cincinnati, Cincinnati, OH, 45221 ***Professor***, Department of Chemical and Materials Engineering, 2008-present.

University of Cincinnati, Cincinnati, OH, 45221 ***Associate Professor***, Department of Chemical and Materials Engineering, 2000-2007.

ETHZ, Zurich Switzerland ***Visiting Professor*** Funded by Swiss National Science Foundation and Dupont Corporation. 8/2003-8/2004.

University of Cincinnati, Cincinnati, OH, 45221 ***Assistant Professor***, Department of Materials Science and Engineering, 1994-2000.

Sandia National Laboratory, Albuquerque, NM 87185, ***Staff Member***, Organic Materials Group 1815. Cooperative research agreements with U.S. industrial partners. 1993-1994.

US Patent and Trademark Office, Arlington, VA. Patent Examiner Biomedical Materials. 1982-1986.

Other Experience and Professional Memberships

2008 Fellow American Physical Society
2000-2008 Advisory Board Intense Pulse Neutron Source, Argonne Natonal Laboraotry.
2003-present Founding Member of LENS Neutron Scattering Facility at Indiana University
2000-present Founding Member of LSU Synchrotron CAMD SAXS User Group
1980-present Member American Institute of Chemical Engineers
1990-present Member American Physical Society
1992-present Member American Crystallographic Society
2004-2005 Chair of the Small Angle Scattering Special Interest Group ACryS.
2003-2004 Program Chair Small Angle Scattering Special Interest Group ACryS
1995-present Panel and Individual Referee for NSF/PRF/DOE/Commerce Proposals.

10 Related Publications (from 113 peer reviewed H-Index 25)

1) *Towards resolution of ambiguity for the unfolded state.* Beaucage G *Biophysical J.* **95** 503-509 (2008).
2) *Probing the dynamics of nanoparticle growth in a flame using synchrotron radiation.* Beaucage G, Kammler HK, Mueller R, Strobel R, Agashe N, Pratsinis SE and Narayanan T, *Nature Mater.* **3,** 370-373 (2004).
3) *In situ studies of nano-particle growth dynamics in premixed flames.* Kammler HK, Beaucage G, Kohls DJ, Agashe N. Ilavsky J., *J Appl. Phys.* **97**(5) 2005 (Article 054309).
4) *3D Hierarchical orientation in polymer-clay nanocomposite films.* Bafna A, Beaucage G, Mirabella F *Polymer* **44**, 1103-1115 (2003).
5) *A structural model for equilibrium swollen networks.* Sukumaran SK, Beaucage G *Europhysics Letters* **59** 714-720 (2002).
6) *Approximations leading to a unified exponential/power-law approach to small-angle scattering.* Beaucage G, *J. Appl. Crystallogr.* **28**, 717-728 (1995).
7) *Small-Angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension.* Beaucage G, *J. Appl. Crystallogr.* **29**, 134-146 (1996).
8) *Determination of branch fraction and minimum dimension of mass-fractal aggregates.* Beaucage G, *Phys. Rev. E*, **70**, 031401 (2004).
9) *Quantification of branching in disordered materials.* Kulkarni A, Beaucage G *J. Polym. Sci. Polym. Phys.* **44** 1395-1405 (2006).
10) *Persistence Length of Short-Chain Branched Polyethylene* Ramachandran R, Beaucage G, Kulkarni AS, McFaddin D, Merrick-Mack J, Galiatsatos V *Macromolecules* In Press (11/2008).

Synergistic Activities

1) *Creation*: Development of scattering theories (the unified function) to describe aggregate

nanostructures, biopolymers, branched structures [1-4,6-10]. *Integration:* Pioneered application of x-ray scattering in situ to pyrolytic synthesis of nanomaterials [2,3]. *Transfer of Knowledge*: Developed and co-developed user software for the analysis of scattering data using the unified function with Jan Ilavsky.

2) *Creation*: Developed aero-sol-gel reactor for room temperature aerosol synthesis.

3) Transfer of Knowledge: Chairman of small-angle scattering group American Crystallographic Association, Organizer for annual meeting of ACA.

4) *Transfer of Knowledge*: Organizer for characterization session in particle technology for AIChE meeting Fall 2005, and Spring (World Particle Congress) 2006. Organizing session on in situ characterization for Fall 2006 AICHE meeting in San Francisco. Organized three sessions for AIChE in Philadelphia 100'th Anniversary Annual Meeting 2008.

5) *Transfer of Knowledge*: 12 web courses (9 pertaining to polymers) extensive notes, lab experiments and data. 235,000 different IP#'s have hit this course suite since 2000 (averaging >70 IP hits/day).

Collaborators & Other Affiliations (past 48 months)

Dr. J. A. van Bokhoven, Professor, ETH, Chem. and Bioengineering, Zurich, Switzerland.

Dr. J. Ilavsky, UNICAT, APS, Argonne National Laboratories, Argonne Illinois.

Dr. F. Mirabella, Independent Consultant, Fort Myers Flordia.

Dr. T. Narayanan, ESRF ID02, Grenoble France.

Dr. S. E. Pratsinis, Process Engineering, ETHZ, Zurich, Switzerland.

Dr. S. K. Sukumaran, Assistant Professor, Yamamoto University Japan.

Dr. T. Trevoort, Materials Science, ETHZ, Zurich Switzerland.

Vassilios Galiatsatos, Senior Scientist, LyodellBasell Cincinnati OH

Peter Smirnoitis, Professor Chemical Engineering, University of Cincinnati

David Britton, Professor Physics, University of Cape Town, South Africa

Graduate & Postdoctoral Advisors

Dr. Richard S. Stein, Emeritus Professor of Polymer Science and Engineering, University of Massachusetts, Amherst, MA. Member NAS and NAE.

Dr. D. W. Schaefer, Professor of Engineering (Formerly Dean of Engineering), U. Cincinnati. Post-doc was with Schaefer and John Curro at Sandia National Laboratory.

Dr. J. G. Curro, Former Head of Polymer Group, Sandia National Laboratory, Albuquerque NM.

Thesis Advisor and Postgraduate-Scholar Sponsor (PhD: 7 , MS: 8, Post Doc: 2)

Current Students: (4 Graduate Students, 2 Funded REU Undergraduate, 1 funded RET High School Teacher, 2 Unfunded Undergraduates)

Durgesh Rai: PhD studies scattering theory.

Sachit Chopras: PhD studies flame-made nanoparticles for nano-catalysts and other applications. Funded by NSF CTS.

Ramnath Ramachandran: PhD studies branching and persistence effects on rheology in polyolefins. Funded by LyondellBasell.

Ryan Breese (MS 2004; PhD 2009): PhD studies on oriented polymer film structure/property relationships. Funded by Equistar and now by Eclipse Film Technologies.

Mangesh Champhekar: (MS 11/2008) Studies of ultra oriented polyolefin/clay nano-composites.

Hao Liu, Senior Project: In situ SAXS studies of Diesel Exhaust at the CHESS Synchrotron.

Kurt Woodford, *Senior Project: Orientation in Polyolefin Films.*

Undergraduate Research Assistant (NSF REU Students): Stephanie Berger, Carbon coated silica for solar cell applications. **Robin Holland,** (Minority REU Student) In situ studies of diesel exhaust nanoparticulates using synchrotrons. **Maesa Idries**, Current REU student.

High School Teacher (NSF RET Participant): Edwin Segbefia Princeton High School Physics Department (Minority teacher). Flame-made hematite nano-particles for arsenic remediation in drinking water.

Select Past Graduated Students/Post Doc

Amit Kulkarni (MS 2004; PhD 2007): Funded by P&G, Intel, Equistar. Currently Research Engineer *GE Plastics Evansville IN (10/2007).*

Doug Kohls, (MS 2002; PhD 2006): Currently Assistant Professor Dept. Materials Science and Engineering University of Cincinnati.

Hashard Chavan (MS 2006) *Bioplastics San Jose CA.*

Ayush Bafna (PhD 2004, MS 2002) *Research Engineer, Dow Chemical Central Research Freeport TX.*

Nikhil Agashe (PhD 2004, MS 2001) *Research Engineer GE Plastics, Evanston IN.*

Suresh Murugesan (PhD Chemistry 2003) *Scientist Texas Research Institute.*

S. Sukumaran (PhD 2002) *Asst. Prof. Polymer Science Yamata University, Japan.*

G. Skillas (Post-Doc from ETH Zurich 2001) *Research scientist, GMX Degussa, Hanau Germany.*

J. Hyeon-Lee (PhD 1998) *Research Scientist, Samsung Research Institute, Seoul, South Korea.*

Ling Guo (MS 1997) *P&G Miami Valley Laboratories (Central Research Division).*

S. Rane (PhD 1999) *Senior Research Engineer, Procter& Gamble Beckett Ridge Technical Center Cincinnati.*

SUMMARY PROPOSAL BUDGET

YEAR 1

ORGANIZATION **University of Cincinnati Main Campus**	FOR NSF USE ONLY PROPOSAL NO.	DURATION (months) Proposed	Granted
PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR **Gregory Beaucage**	AWARD NO.		

A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	NSF Funded Person-months CAL	ACAD	SUMR	Funds Requested By proposer	Funds granted by NSF (if different)
1. **Gregory Beaucage - Professor**	0.00	0.00	0.81	$ **10,410**	$
2.					
3.					
4.					
5.					
6. (**0**) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00	**0**	
7. (**1**) TOTAL SENIOR PERSONNEL (1 - 6)	0.00	0.00	0.81	**10,410**	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (**1**) POST DOCTORAL SCHOLARS	12.00	0.00	0.00	**50,000**	
2. (**0**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	0.00	0.00	0.00	**0**	
3. (**1**) GRADUATE STUDENTS				**25,000**	
4. (**0**) UNDERGRADUATE STUDENTS				**0**	
5. (**0**) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				**0**	
6. (**0**) OTHER				**0**	
TOTAL SALARIES AND WAGES (A + B)				**85,410**	
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)				**17,934**	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				**103,344**	

D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)			
Dynamic Light Scattering Camera	**$ 50,000**		
Shear Rheometer	**30,000**		
TOTAL EQUIPMENT		**80,000**	
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)		**21,000**	
2. FOREIGN		**31,500**	
F. PARTICIPANT SUPPORT COSTS			
1. STIPENDS	$ **6,000**		
2. TRAVEL	**18,000**		
3. SUBSISTENCE	**0**		
4. OTHER	**0**		
TOTAL NUMBER OF PARTICIPANTS (**2**)	TOTAL PARTICIPANT COSTS	**24,000**	
G. OTHER DIRECT COSTS			
1. MATERIALS AND SUPPLIES		**8,000**	
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION		**200**	
3. CONSULTANT SERVICES		**0**	
4. COMPUTER SERVICES		**0**	
5. SUBAWARDS		**0**	
6. OTHER		**5,590**	
TOTAL OTHER DIRECT COSTS		**13,790**	
H. TOTAL DIRECT COSTS (A THROUGH G)		**273,634**	
I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) **F&A on MTDC (Rate: 26.0000, Base: 166544) (Cont. on Comments Page)**			
TOTAL INDIRECT COSTS (F&A)		**44,801**	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)		**318,435**	
K. RESIDUAL FUNDS		**0**	
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)		$ **318,435**	$
M. COST SHARING PROPOSED LEVEL $ **0**	AGREED LEVEL IF DIFFERENT $		

PI/PD NAME **Gregory Beaucage**	FOR NSF USE ONLY INDIRECT COST RATE VERIFICATION		
ORG. REP. NAME*	Date Checked	Date Of Rate Sheet	Initials - ORG

***ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET**

SUMMARY PROPOSAL BUDGET COMMENTS - Year 1

**** I- Indirect Costs**
REU & RET 25% of Stipends (Rate: 25.0000, Base 6000)

SUMMARY YEAR 2
PROPOSAL BUDGET

	FOR NSF USE ONLY		
ORGANIZATION **University of Cincinnati Main Campus**	PROPOSAL NO.	DURATION (months)	
		Proposed	Granted
PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR **Gregory Beaucage**	AWARD NO.		

A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	NSF Funded Person-months CAL	ACAD	SUMR	Funds Requested By proposer	Funds granted by NSF (if different)
1. **Gregory Beaucage - Professor**	0.00	0.00	0.81	$ **10,722**	$
2.					
3.					
4.					
5.					
6. (**0**) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00	**0**	
7. (**1**) TOTAL SENIOR PERSONNEL (1 - 6)	0.00	0.00	0.81	**10,722**	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (**1**) POST DOCTORAL SCHOLARS	12.00	0.00	0.00	**51,500**	
2. (**0**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	0.00	0.00	0.00	**0**	
3. (**1**) GRADUATE STUDENTS				**25,750**	
4. (**0**) UNDERGRADUATE STUDENTS				**0**	
5. (**0**) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				**0**	
6. (**0**) OTHER				**0**	
TOTAL SALARIES AND WAGES (A + B)				**87,972**	
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)				**18,782**	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				**106,754**	
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)					
TOTAL EQUIPMENT				**0**	
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				**21,630**	
2. FOREIGN				**23,690**	
F. PARTICIPANT SUPPORT COSTS 1. STIPENDS $ **6,180** 2. TRAVEL **17,210** 3. SUBSISTENCE **0** 4. OTHER **0**					
TOTAL NUMBER OF PARTICIPANTS (**2**) TOTAL PARTICIPANT COSTS				**23,390**	
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES				**8,240**	
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				**206**	
3. CONSULTANT SERVICES				**0**	
4. COMPUTER SERVICES				**0**	
5. SUBAWARDS				**0**	
6. OTHER				**5,758**	
TOTAL OTHER DIRECT COSTS				**14,204**	
H. TOTAL DIRECT COSTS (A THROUGH G)				**189,668**	
I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) **F&A on MTDC (Rate: 26.0000, Base: 163095) (Cont. on Comments Page)**					
TOTAL INDIRECT COSTS (F&A)				**43,950**	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)				**233,618**	
K. RESIDUAL FUNDS				**0**	
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				$ **233,618**	$

M. COST SHARING PROPOSED LEVEL $ **0**	AGREED LEVEL IF DIFFERENT $		
PI/PD NAME **Gregory Beaucage**	FOR NSF USE ONLY INDIRECT COST RATE VERIFICATION		
ORG. REP. NAME*	Date Checked	Date Of Rate Sheet	Initials - ORG

***ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET**

SUMMARY PROPOSAL BUDGET COMMENTS - Year 2

**** I- Indirect Costs**
REU & RET 25% of Stipends (Rate: 25.0000, Base 6180)

SUMMARY PROPOSAL BUDGET

YEAR 3

ORGANIZATION **University of Cincinnati Main Campus**	**FOR NSF USE ONLY** PROPOSAL NO.	DURATION (months) Proposed	 Granted
PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR **Gregory Beaucage**	AWARD NO.		

A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	NSF Funded Person-months CAL	ACAD	SUMR	Funds Requested By proposer	Funds granted by NSF (if different)
1. **Gregory Beaucage - Professor**	0.00	0.00	0.81	$ **11,044**	$
2.					
3.					
4.					
5.					
6. (**0**) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00	**0**	
7. (**1**) TOTAL SENIOR PERSONNEL (1 - 6)	0.00	0.00	0.81	**11,044**	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (**1**) POST DOCTORAL SCHOLARS	12.00	0.00	0.00	**53,045**	
2. (**0**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	0.00	0.00	0.00	**0**	
3. (**1**) GRADUATE STUDENTS				**26,523**	
4. (**0**) UNDERGRADUATE STUDENTS				**0**	
5. (**0**) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				**0**	
6. (**0**) OTHER				**0**	
TOTAL SALARIES AND WAGES (A + B)				**90,612**	
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)				**19,667**	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				**110,279**	
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)					
TOTAL EQUIPMENT				**0**	
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				**22,279**	
2. FOREIGN				**24,401**	
F. PARTICIPANT SUPPORT COSTS 1. STIPENDS $ **6,365** 2. TRAVEL **17,426** 3. SUBSISTENCE **0** 4. OTHER **0**					
TOTAL NUMBER OF PARTICIPANTS (**2**) TOTAL PARTICIPANT COSTS				**23,791**	
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES				**8,487**	
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				**212**	
3. CONSULTANT SERVICES				**0**	
4. COMPUTER SERVICES				**0**	
5. SUBAWARDS				**0**	
6. OTHER				**5,930**	
TOTAL OTHER DIRECT COSTS				**14,629**	
H. TOTAL DIRECT COSTS (A THROUGH G)				**195,379**	
I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) **F&A on MTDC (Rate: 26.0000, Base: 168310) (Cont. on Comments Page)**					
TOTAL INDIRECT COSTS (F&A)				**45,352**	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)				**240,731**	
K. RESIDUAL FUNDS				**0**	
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				$ **240,731**	$

M. COST SHARING PROPOSED LEVEL $ **0** AGREED LEVEL IF DIFFERENT $

PI/PD NAME **Gregory Beaucage**	**FOR NSF USE ONLY** INDIRECT COST RATE VERIFICATION		
ORG. REP. NAME*	Date Checked	Date Of Rate Sheet	Initials - ORG

***ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET**

SUMMARY PROPOSAL BUDGET COMMENTS - Year 3

**** I- Indirect Costs**
REU & RET 25% of Stipends (Rate: 25.0000, Base 6365)

SUMMARY PROPOSAL BUDGET

Cumulative

	FOR NSF USE ONLY		
ORGANIZATION **University of Cincinnati Main Campus**	PROPOSAL NO.	DURATION (months)	
		Proposed	Granted
PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR **Gregory Beaucage**	AWARD NO.		

A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	NSF Funded Person-months CAL	ACAD	SUMR	Funds Requested By proposer	Funds granted by NSF (if different)
1. **Gregory Beaucage - Professor**	0.00	0.00	2.43	$ **32,176**	$
2.					
3.					
4.					
5.					
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00	**0**	
7. (**1**) TOTAL SENIOR PERSONNEL (1 - 6)	0.00	0.00	2.43	**32,176**	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (**3**) POST DOCTORAL SCHOLARS	36.00	0.00	0.00	**154,545**	
2. (**0**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	0.00	0.00	0.00	**0**	
3. (**3**) GRADUATE STUDENTS				**77,273**	
4. (**0**) UNDERGRADUATE STUDENTS				**0**	
5. (**0**) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				**0**	
6. (**0**) OTHER				**0**	
TOTAL SALARIES AND WAGES (A + B)				**263,994**	
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)				**56,383**	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				**320,377**	
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.) **$ 80,000**					
TOTAL EQUIPMENT				**80,000**	
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				**64,909**	
2. FOREIGN				**79,591**	
F. PARTICIPANT SUPPORT COSTS 1. STIPENDS $ **18,545** 2. TRAVEL **52,636** 3. SUBSISTENCE **0** 4. OTHER **0**					
TOTAL NUMBER OF PARTICIPANTS (**6**) TOTAL PARTICIPANT COSTS				**71,181**	
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES				**24,727**	
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				**618**	
3. CONSULTANT SERVICES				**0**	
4. COMPUTER SERVICES				**0**	
5. SUBAWARDS				**0**	
6. OTHER				**17,278**	
TOTAL OTHER DIRECT COSTS				**42,623**	
H. TOTAL DIRECT COSTS (A THROUGH G)				**658,681**	
I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE)					
TOTAL INDIRECT COSTS (F&A)				**134,103**	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)				**792,784**	
K. RESIDUAL FUNDS				**0**	
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				$ **792,784**	$

M. COST SHARING PROPOSED LEVEL $ **0**	AGREED LEVEL IF DIFFERENT $		
PI/PD NAME **Gregory Beaucage**	**FOR NSF USE ONLY** INDIRECT COST RATE VERIFICATION		
ORG. REP. NAME*	Date Checked	Date Of Rate Sheet	Initials - ORG

C ***ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET**

Budget Justification

PERSONNEL:

The project will support a postdoctoral student ($50,000) who will work in Moscow learning synthetic techniques at the Moscow State University. The project will support the PI for 25% of the summer ($10,410) when he will travel to Moscow to work on the project with Prof. Ilya Nifant'ev's group and with LyondellBasell Researchers in Frankfurt, Germany and Ferrara, Italy. The remainder of the PI's billable time will be spent at neutron scattering facilities in the US. The project also supports a graduate student ($25,000) who will spend 25% of his time at Cincinnati and 75% of his time either in Moscow, Frankfurt and Ferrara Italy or at neutron scattering facilities in the US (Oak Ridge and NIST). An undergraduate student ($6,000) on an REU supplemental will work 25% of his/her time at UC and 75% of the time in Moscow or at neutron scattering facilities. The project also funds a RET high school chemistry teacher who will spend one month (all of his funded time) at Moscow State University in the summer (RET covers only travel not stipend).

Annual increases for the PI are budgeted according to the AAUP contract. Increases of 3% in years 2 and 3 are included for the graduate student, post doc and undergraduate REU student.

FRINGE BENEFITS:

Fringe Benefits are a direct-charge as a percentage of salaries and wages at rates established by the university, and reviewed annually by DHHS, for salary expenses. Fringe Benefits amount to $16,552, $18,647, and $19,527 for the three years of proposed funding.

EQUIPMENT: (100% on-campus charges)

The proposal will purchase two new instruments in the lab of Beaucage that will be used in the project to complement existing facilities. A dynamic light scattering instrument, $50,000, will be used to develop comparative measures of structural topology for the polymers developed in the project. A shear rheometer, $30,000, will be used to determine the consequence of topological features on the physical properties of the materials synthesized.

TRAVEL: (100% off-campus charges)

The project will involve significant amounts of travel between Cincinnati and Moscow as well as travel to national user facilities in the US for neutron scattering measurements. Some support for traveling to meetings such as the American Chemical Society Meeting is also included. Amounts listed below are for the first year and an increase of 3% is budgeted for years 2 and 3. A dorm room at Moscow State University costs $250/week and $50/day for food is allocated for the graduate student and undergraduate in addition to their stipends while they stay in Moscow. Airfare is about $2000 from Cincinnati to Moscow. A 10-week visit is estimated to cost $8,000 for a student. The high school teacher, postdoctoral researcher and professor will stay in hotels with an associated higher travel cost.

Post Doc:

Foreign Travel:

The budget includes travel between Moscow and the US two times per year (@ $2,000 airfare, 10 days housing and food $2,000) as well as travel to Germany and Italy @

$3,000 per trip. $1,000 for airfare within Europe and $2,000 for housing/food for a total of $11,000.

Domestic Travel:

The post-doc will travel to one meeting per year at $3,000 ($700 Registration, Hotel $700, Airfare $1,000, Food $300).

REU Student:

Foreign Travel:

The REU student will travel to Moscow for 10 weeks at the student rates noted above $8,000 in year 1.

No Foreign travel in years 2 and 3 for REU student.

Domestic Travel:

No Domestic travel in year 1 for REU student.

The REU student will attend one meeting per year at $3,000 in years 2 and 3.

The REU student will travel to national user facilities in the US for neutron scattering on 2 trips at about $2,000 per trip.

Total Domestic REU travel is $7,000/year in years 2 and 3.

Graduate Student:

Foreign Travel:

The graduate student will travel to Moscow for 10 weeks at the student rates noted above $8,000 in year 1.

Plus travel to Germany and Italy at about $1,500.

Total graduate student foreign travel first year $9,500.

In year 2 and 3 the graduate student will take one trip to MSU for about 10 days plus travel to Germany and Italy for a total of $5,500.

Total graduate student foreign travel $5,500 years 2 and 3.

Domestic Travel:

The graduate student will travel for one meeting per year at $3,000, and travel to National User Facilities for Neutron Scattering 3 times per year at $6,000/yr.

Total Domestic Graduate Student is $9,000 in years 1, 2 and 3.

Principle Investigator:

Foreign Travel:

The PI will travel to Moscow/Italy and Germany for 4 weeks in the summer for year 1. Airfare $3000 Housing/food @ ~$250/day ($8000).

Total PI Foreign ~$11,000 year 1.

In years 2 and 3 the PI will travel to MSU/Italy and Germany for 2 weeks.

$6,500/yr in years 2 and 3.

Domestic Travel:

PI will travel to one meeting for $3,000 and to National User Facilities for neutron scattering (3 trips) $6,000/yr.

Total Domestic for PI: $9,000

Supplies and other Direct Costs: (100% on-campus charges)

Materials and supplies: $8,000. Analytic Services $2,500. Publications $200. A part of the graduate student tuition is also charged at $3090 for the first year which increments as a fraction of planned tuition increases.

Total Supplies and Direct Costs: $13,790 for the first year.

Amounts listed are for the first year and an increase of 3% is budgeted for years 2 and 3. Analytic services will be used for services such as use of analytic services 25% at the UC Characterization Center, mass spectrometers and other spectrometers in the Chemistry Department as well as the Engineering and Physics Machine Shops through university approved service centers. Rates at approved service centers are approved by the university council for service centers in accordance with federal regulations. 75% will be used for off campus services.

Tuition is included for the graduate student at $3,090 for the first year and increasing at 3% annually for a total of $9,551 as mandated by the University. Tuition is charged at a reduced rate that represents a savings of about $12,000 per year.

About $200 per year is included for publication and reprint charges, with an increase of 3% included for years 2 and 3.

REU BUDGET (Research Experience for Undergraduates):

Amounts listed below are for the first year and an increase of 3% is budgeted for years 2 and 3. 25% indirect charges are taken on the stipend of these expenses as specified by the NSF.

Foreign travel $8,000 (Year 1)
Domestic travel $7,000 (Year 2 and 3)
Stipend: $6,000

RET BUDGET (Research Experience for Teachers): (100% off-campus)

Each year one high school teacher will be sent to Moscow State University from the Cincinnati Area Chemistry teachers. There will be no stipend so the traditional RET indirect charge of 25% of the stipend is not be included. The $10,000 RET funding will be used entirely to fund travel for about 1 month in Moscow. The RET participant will travel to Moscow for a month in the summer: Airfare $2000 Housing/food @ $250/day ($8000). (Since it is difficult to estimate travel costs accurately, any funds not used for travel from the RET part of the budget will be given to the high school teacher as a stipend and charged an indirect rate of 25% or will be used to supply the high school teacher with equipment to perform labs related to the project at his/her home institution.)

Total RET Foreign $10,000. Where the daily allowance for food and housing is based on (but lower than) the US State Department Allowable Rates for Moscow. The teacher will participate in research at Moscow State University and will also participate in a teaching enhancement program in the Teaching College of MSU.

INDIRECT COSTS:

Indirect costs are charged at 26.0% of Modified Total Direct Costs (MTDC) for greater than 51% off-campus expenses per DHHS rate agreement dated 06/11/09, excluding equipment, tuition and REU travel and stipend costs. The REU and RET portion of this request are charged at a flat rate of 25% on stipends only.

Current and Pending Support

(See GPG Section II.C.2.h for guidance on information to include on this form.)

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.

Investigator: Gregory Beaucage

Other agencies (including NSF) to which this proposal has been/will be submitted.

Support: ☐ Current ☒ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: International Collaboration in Chemistry: New polyolefin architectures via advanced catalysts and customized chain control agents (THIS PROPOSAL)

Source of Support: NSF
Total Award Amount: $ 792,785 Total Award Period Covered: 09/01/10 - 08/31/13
Location of Project: University of Cincinnati/Moscow State University
Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 0.81

Support: ☐ Current ☒ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: Materials World Network: Tuned oxide nanopartiles for solar cells in sub-Saharan Africa.

Source of Support: NSF
Total Award Amount: $ 465,277 Total Award Period Covered: 06/01/10 - 05/31/13
Location of Project: University of Cincinnati/Cape Town University, South Africa
Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 0.78

Support: ☐ Current ☒ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: Nanomechanics of Complex Structures

Source of Support: NSF
Total Award Amount: $ 370,202 Total Award Period Covered: 02/01/10 - 01/31/13
Location of Project: University of Cincinnati
Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 0.50

Support: ☐ Current ☒ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: High Temperature WGS Catalysts (Peter Smirnoitis PI, Beaucage part $20,000)

Source of Support: NSF
Total Award Amount: $ 20,000 Total Award Period Covered: 02/01/10 - 01/31/13
Location of Project: University of Cincinnati
Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 0.25

Support: ☒ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: Construction of USAXS Camera

Source of Support: Procter & Gamble
Total Award Amount: $ 20,000 Total Award Period Covered: 06/01/09 - 06/01/10
Location of Project: University of Cincinnati
Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Summ: 0.00

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*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

Current and Pending Support

(See GPG Section II.C.2.h for guidance on information to include on this form.)

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.

Investigator: Gregory Beaucage

Other agencies (including NSF) to which this proposal has been/will be submitted.

Support: ☒ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: Structural Studies of Commercial Polyolefins

Source of Support: LyondellBasell
Total Award Amount: $ 316,052 Total Award Period Covered: 09/01/06 - 08/31/10
Location of Project: University of Cincinnati
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.00 Sumr: 0.50

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:

Source of Support:
Total Award Amount: $ Total Award Period Covered:
Location of Project:
Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
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Total Award Amount: $ Total Award Period Covered:
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Person-Months Per Year Committed to the Project. Cal: Acad: Summ:

*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

USE ADDITIONAL SHEETS AS NECESSARY

Facilities, Other Resources and Equipment

Cincinnati

Facilities:

Beaucage/University of Cincinnati:

410 Rhodes Hall Laboratory is a 600 square foot research laboratory primarily focusing on scattering and polymer characterization instruments.

551 Engineering Research Center Laboratory is a 300 square foot research laboratory with a hood, suitable for chemical synthesis. A light scattering camera is also housed in this lab as well as two polymer-processing machines.

Office: Beaucage's office is located in 492 Rhodes Hall with student desks in 410B Rhodes and in the laboratory.

Equipment:

Beaucage/University of Cincinnati:

Polymer Processing Equipment:

Collin Teach Machine Direction Orientation Unit On loan from Eclipse Film Technology and Collin GmbH (http://www.drcollin.de/en/index_en.html). Lab scale polymer film stretching machine.

Brabender 50 gm Extruder Located in ERC 551 Lab. Film blowing attachment and home made take-up tower as well as mixing head. Home made fiber spinning apparatus. (See http://www.eng.uc.edu/~gbeaucag/Classes/Processing.html for pictures and video of this equipment. Equipment was donated by Dow Chemical and P&G to Beaucage, is very old but functional.

Departmental Carver Hot Press. Located in Polymer Processing Laboratory.

TM Long Stretch Polymer Film Biaxial Stretcher from Inventure Labs www.inventurelabs.com. Donated from P&G Polymer Processing Center Beckett Ridge Laboratories to Beaucage. Instrument is for static and dynamic precision biaxial deformation of polymer films. This instrument will be used to study post blowing/casting nano-composite orientation located in 410 Rhodes Hall.

Departmental Battenfeld injection molding machine. Fairly old but functional machine purchased second hand about 10 years ago for $7,000. Located in Polymer Processing Laboratory at the University of Cincinnati.

Scattering Equipment

12 kW Rigaku rotating anode X-ray source with three small angle X-ray scattering cameras located in 410 Rhodes Hall laboratory of Beaucage with:

A pinhole camera with a 2-D detector focusing optics automatic sample changer. Instrument has been widely used in published SAXS studies. 0.5 to 50 nm size resolution, absolute intensity capability.

Kratky SAXS camera, capable of wider q-range compared to pinhole camera. Data is slit smeared requiring desmearing making results less reliable. 0.1 to 100 nm resolution.

Bonse-Hart USAXS camera. 1 nm to 1 micron resolution.

Two static light scattering cameras and optical components.

Pinhole static small-angle light scattering camera with 2D CCD camera located in 410 Rhodes Hall laboratory of Beaucage. Camera is enclosed in a dark box with vertical alignment, 20 mW HeNe laser, adjustable attenuator, polarizers pinhole optics, hot stage capabilities, scattering is projected on a screen and imaged with a Princeton Instruments 2D CCD detector. 0.6 to 100 micron resolution.

Ultra-small angle static light scattering camera located in 551 Engineering Research Center laboratory of Beaucage. 30 mW HeNe laser, step scan goniometer with fiber optics connection to PMT and computer. Unique optics for USALS measurements, 1 micron to 1 cm resolution.

Assorted optics, optical tracks, 5 mW HeNe laser, stepper motors and motor controller.

Other Equipment:

Dupont Instruments 912 Differential Scanning Calorimeter in the 410 Rhodes Lab.

TA Instruments Dynamic Mechanical Analyzer DMA 983 in the 410 Rhodes Lab.

4 Pyrolytic reactors with 6 mass flow controllers, assorted tubing, heat tape, neutralizers, filter banks and exhaust pump located in the 551 Engineering Research Center Laboratory of Beaucage.

The Advanced Materials Characterization Center (AMCC) operated by the Department of Chemical and Materials Engineering at University of Cincinnati Located on the 3'rd floor of the Engineering Research Center has a CM-20 TEM, with a LaB_6 source, theoretical resolution of 1.4 Å and EDS capabilities. The operating costs are $85 per hour.

The SEM setup at the University of Cincinnati AMCC facility include a Hitachi S 4000 conventional FEG SEM with a theoretical resolution of 15 Å, and EDS capabilities and an environmental FEI XL 30 ESEM-FEG with a theoretical resolution of 15 Å and operating pressure of 20 torr. The operating costs for SEM are $80 per hour.

X-ray powder diffraction is also available at the AMCC with a user fee or $40/h.

Other Resources:

Beaucage is a long-term collaborator and consultant with the Equistar division of LyondellBasell Corporation, the number 2 producer of polymers in the US and number 1 producer of polyolefins. Equistar's polymer processing research facility frequently collaborates with Beaucage and this collaboration is expected to continue through this project.

Beaucage is also a long term collaborator and consultant with Procter & Gamble Corporation which has polymer processing facilities in two main locations in Cincinnati.

Beaucage has a working arrangement with two beam lines at the Advanced Photon Source in Chicago at the UNICAT and at the BESSRC user facilities.

SAXS measurements are performed at CHESS (Cornell University) and at SSRL (Stanford University). Beaucage is also a founding member of the user group for the LSU SAXS facility funded by NSF (CAMD).

SANS measurements are performed at HFIR facility of Oak Ridge National Laboratory where Beaucage has consistently obtained beam time for 3 years. Similarly Beaucage has consistently obtained beamtime at NIST's Reactor Division over the past 3 years. SANS time is also available at Los Alamos National Laboratory and through special arrangements at ANSTO at the Bragg Institute in Australia among other international facilities.

Moscow

Facilities:

Nifant'ev/Moscow State University:

431, 532 and H35A Rooms of about 150 square meters research laboratories primarily focusing on synthesis of organic and metalloorganic compounds is located in the building of Department of Chemistry.

Office: Nifant'ev's office is located in H35A Room.

Equipment:

Nifant'ev/Moscow State University:

The team has all necessary small equipment to carry out of the research work of Synthesis of Organic and Metalloorganic compounds:

- Glassware;
- Pumps;
- Stirrers;
- Balances etc.

The Department of Chemistry has all analytical equipment necessary to support the research work of Synthesis of Organic and Metalloorganic compounds:

- 2 NMR spectrometers of 400MHz and 600MHz (Bruker);
- Mass-spectrometers;
- Gas Chromatograph;
- IR spectrometer

Information Pertinent to Prof. Ilya Eduardovich Nifant'ev

Foreign investigator's budget request from the RFFR:

The requested amount from the Russian Foundation for Fundamental Research (RFFR) is 700,000 Rubles (~ 25,000 USD) per 3 years (15% overheard; 45% travel expenses; 40% reagents and supplies).

Current and pending support list

- Olefin polymerization catalysts
  Long term research agreement with Basell Polyolefine GmbH () renewed annually.
  ~ 100,000 USD per year
  This research is limited to conventional Ziegler Natta and metallocene Catalysts so is distinguished from the proposed research. The use of chain transfer agents to produce new chain microstructure and topologies has not been previously considered by either of the PI's or LyondellBasell. The proposed research is a new direction for both of the PI's.
- Co-contributor in RFFR grant "09-03-12232" "Carbon-based polyolefin nanomodifiers"; 2009-2010 with a total budget of 12,000 USD.

2 Page CV Follows:

Ilya Eduardovich Nifant'ev, **Professor**
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Moscow, 119991 Russia

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Education

1970-1980 - graduated from secondary school in Moscow;

1980-1985 - graduated from the Moscow State University, Department of Chemistry M.S. Chemistry;

1985-1988 - Moscow State University, Department of Chemistry, ***Post graduate study***, in the lab of Organometallic Chemistry, ***Ph.D. Organometallic chemistry***.

Advisor: Prof. Dmitri.A.Lemenovskii. "The ways of bis-metallocenes formation"

1988-1992 Moscow State University, Department of Chemistry; ***Post Doctoral Fellow*** the lab of NMR, ***Dr. of Sciences (chemistry)***

Advisor: Prof. Yuri.A.Ustynyuk. "Design and synthesis of cyclopentadienyl-substituted complexes of early transition metals"

Appointments

Moscow State University, Professor, Department of Chemistry, 2004-present.
Moscow State University, Senior scientist, Department of Chemistry, 1992-2004
Moscow State University, Scientist, Department of Chemistry, 1988-1992

Other Experience and Professional Memberships

1982-present Member The Mendeleev Russian Chemical Society
2008-present Panel and Individual Referee for ROSNANO Proposals.

10 Related Publications (from 81 peer reviewed)

1. Highly regiospesific zirconocene catalysts for the isospecific polymerization of propene, Resconi L., Piemontesi F., Camurati I., Sudmeijer O., Nifant'ev I.E., Ivchenko P.V., Kuz'mina L.G., *J.Am.Chem.Soc.*, **1998**, *120*, 2308-2321
2. C2-Symmetric zirconocenes for high molecular weight amorphous polypropylene, Angeli D., Balboni D., Baruzzi G., Braga V., Camuratti I., Moscardi G., Piemontesi F., Resconi L., Nifant'ev I., Guerra G., Venditto V., Antinucci S., *Macromolecular Chemistry and Physics*, **2001**, 202, 2010
3. A DFT study of ethylene polymerization by zirconocene-boron catalytic systems. The effect of counterion on the kinetics and mechanism of the process, Nifant'ev, I.E.; Ustynyuk, L.Yu.; Laikov, D.N., *Organometallics,* **2001**, *20*, 5375-5393
4. Fluorenyltitanium triisopropoxide and bis(fluorenyl)titanium diisopropoxide: a facile synthesis, molecular structure, and catalytic activity, Sergei Ya. Knjazhanski, Gregorio Cadenas, Maricela García, Catalina M. Pérez, Ilya E. Nifanti'ev, Pavel V. Ivchenko, Konstantin A.Lyssenko, *Organometallics*, **2002**, *21*, 3094-3099.

5 Resconi, L.; Guidotti, S.; Camurati, I.; Nifant'ev, I. E.; Laishevtsev, I. *Polym.Mater. Sci. Eng.* **2002**, *87*, 76-77.

6. ansa-Zirconocenes Based on N-Substituted 2-Methylcyclopenta[b]Indoles: Synthesis and Catalyst Evaluation in Liquid Propylene Polymerization, van Baar, J. F.; Horton, A. D.; de Kloe, K. P.; Kragtwijk, E.; Mkoyan, S. G.; Nifant'ev, I. E.; Schut, P. A.; Taidakov, I. V.; *Organometallics*, **2003**; *22*; 2711-2722.

7. Heterocycle-Fused Indenyl Silyl Amido Dimethyl Titanium Complexes as Catalysts for High Molecular Weight Syndiotactic Amorphous Polypropylene, Organometallics, Grandini, C.; Camurati, I.; Guidotti, S.; Mascellani, N.; Resconi, L.; Nifant'ev, I. E.; Kashulin, I. A.; Ivchenko, P. V.; Mercandelli, P.; Sironi, A.; *Organometallics*, **2004**; *23*; 344-360.
8. C_1-symmetric heterocyclic zirconocenes as catalysts for propylene polymerization, Ilya E. Nifant'ev, Ilya Laishevtsev, Igor A.Kashulin, Pavel V.Ivchenko, Simona Guidotti, Fabrizio Piemontesi, Isabella Camurati, Luigi Resconi, Peter A.A. Klusener, J.J.H. Rijsemus, K.P. de Kloe, Frans M. Korndorffer, *Macromolecular Chemistry and Physics*, **2004**, *205*, 2275-2291.
9. C1-Symmetric heterocyclic zirconocenes as catalysts for propylene polymerization, L.Resconi, S.Guidotti, I.Camuratti, R.Frabetti, F.Focante, I.Nifant'ev, I.Laishevtsev, *Macromol.Chem.Phys.*, **2005**, *206*, 1405-1438
10. Structure-Property Correlations in Polypropylene from Metallocene Catalysts: Stereodefective, Regioregular Isotactic Polypropylene, De Rosa, C.; Auriemma, F.; Di Capua, A.; Resconi, L.; Guidotti, S.; Camurati, I.; Nifant'ev, I. E.; Laishevtsev, I. P.; *J. Am. Chem. Soc.*; **2004**; *126*; 17040-17049.

Collaborators & Other Affiliations (past 48 months)

Prof. L.A.Novokshenova, head of laboratory, Institut of Chemical Physics RAS, Moscow, Russia

Prof. Yu.A.Ustynyuk, head of laboratory, Department of Chemistry, Moscow State University, Moscow, Russia

Prof. D.A.Lemenovskii, head of laboratory, Department of Chemistry, Moscow State University, Moscow, Russia

Prof. A.L.Maksimov, head of laboratory, Institute of Peprochemical Synthesis RAS, Moscow, Russia

Dr. A.V.Vorogushin, Director of Department, SIBUR, Moscow, Russia

Dr. D.M.Roitershtein, Head of Organic Chemistry Division, Moscow City Teachers' Training University, Moscow, Russia

Prof. A.V.Pshejetsky, Professor, Departments of Pediatrics and Biochemistry University of Montreal

Dr. S.Mihan, Research Manager, Basell GmbH, Germany

Graduate & Postdoctoral Advisors

Prof. Yuri.A.Ustynyuk, Professor, head of laboratory, Department of Chemistry, Moscow State University, Moscow, Russia

Prof. Dmitri.A.Lemenovskii, Professor, head of laboratory, Department of Chemistry, Moscow State University, Moscow, Russia

Thesis Advisor and Postgraduate-Scholar Sponsor:

11 PhD, 15 MS, 5 Post Doc.

Current Students:

3 Graduate Students; 3 Ph.D. students

Awards:

ACS Arthur K. Doolittle Award, 2002

Date: January, 2010

МОСКОВСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ
имени М.В. ЛОМОНОСОВА
LOMONOSOV MOSCOW STATE UNIVERSITY

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29.01.10 № 23-3/102

На: №______ №______

______ №______

Re: №______ №______

The letter of commitment

This letter is to certify that Moscow State University, Department of Chemistry assures that it is committed to the collaboration between Moscow State University (Prof. Ilya E.Nifant'ev) and University of Cincinnati (Prof. Gregory Beaucage) as provided by the joint NSF-RFBR project application ***"New polyolefin architectures via advanced catalysts and customized chain control agents"*** and will give students appropriate access to all necessary facilities of Department of Chemistry.

Prof. Ilya E.Nifant'ev will participate in the project and will assist the American students who will be in Moscow including, Mentoring the Post doc, overseeing the graduate student, undergraduate and the high school teacher for necessary time.

Dean of the Department of Chemistry

Prof. Valery V.Lunin

Postdoctoral Researcher Mentoring Plan

This Postdoctoral Researcher Mentoring Plan has been prepared by Gregory Beaucage at the University of Cincinnati. The Plan establishes guidelines for work to be performed by a Postdoctoral Researcher in support of the NSF International Collaboration in Chemistry Project Awarded to the University of Cincinnati, entitled "***New polyolefin architectures via advanced catalysts and customized chain control agents***". The Postdoctoral Researcher assigned to the project will work in the Moscow State University laboratory in Moscow Russia, at Oak Ridge National Laboratory, at the National Institute of Standards and Technology, at laboratories of LyondellBasell in Frankfurt Germany and Ferrara Italy as well as at the University of Cincinnati and will conduct research on synthesis of advanced catalysts for control of polyolefin microstructure.

1. **Orientation** will include in-depth conversations between Prof. Beaucage, Prof. Nifant'ev, Dr. Sandor Nagy (LyondellBasell) as well as others involved in the project and the Postdoctoral Researcher. Mutual expectations will be discussed and agreed upon in advance. The post-doctoral researcher will work primarily in Moscow so that Prof. Nifant'ev will be principally responsible for setting daily expectations. Orientation topics will include (a) the amount of independence the Postdoctoral Researcher requires, (b) interaction with coworkers, (c) productivity including the importance of scientific publications, (d) work habits and laboratory safety, and (e) documentation of research methodologies and experimental details so that the work can be continued by other researchers in the future. The Postdoctoral Researcher will attend classes in Russian Language given in the Chemistry College at Moscow State University during his/her stay in Moscow with other foreign researchers.
2. **Career Counseling** will be directed at providing the Postdoctoral Researcher with the skills, knowledge, and experience needed to excel in his/her chosen career path. In addition to guidance provided by Profs. Nifant'ev and Beaucage, the Postdoctoral Researcher will be encouraged to discuss career options with researchers and managers at LyondellBasell and with former students and colleagues of Profs. Beaucage and Nifant'ev.
3. **Experience with Preparation of Grant Proposals** will be gained by direct involvement of the Postdoctoral Researcher in proposals prepared by Profs. Beaucage and Nifant'ev. The Postdoctoral Researcher will have an opportunity to learn best practices in proposal preparation including identification of key research questions, definition of objectives, description of approach and rationale, and construction of a work plan, timeline, and budget.
4. **Publications and Presentations** are expected to result form the work supported by the grant. These will be prepared under the direction of Profs. Beaucage and Nifant'ev and in collaboration with researchers at LyondellBasell. The Postdoctoral Researcher will receive guidance and training in the preparation of manuscripts for scientific journals and presentations at conferences.
5. **Teaching and Mentoring Skills** will be developed in the context of regular meetings within Beaucage/Nifant'ev research group during which graduate students and postdoctoral researchers describe their work to colleagues within the group and assist each other with solutions to challenging research problems, often resulting in cross fertilization of ideas. The Post-doc will also teach part of a web based course described in the Project Description as well as mentor a Graduate student and an REU undergraduate student in Moscow.
6. **Instruction in Professional Practices** will be provided on a regular basis in the context of the research work and will include fundamentals of the scientific method, laboratory safety, and other standards of professional practice. In addition, the Postdoctoral Researcher will be encouraged to affiliate with the American Chemical Society and other organizations.
7. **Technology Transfer** activities will include regular contact with researchers at LyondellBasell. The Postdoctoral Researcher will be given an opportunity to become familiar with the university-industry relationship including applicable confidentiality requirements and preparation of invention disclosure applications.
8. **Success of the Mentoring Plan** will be assessed by monitoring the personal progress of the Postdoctoral Researcher through a tracking of the Postdoctoral Researcher's progress toward his/her career goals after finishing the postdoctoral program.

Request for an RET Supplement (3 pages)

1) Overview: Description of the RET activity.

The proposed research experience for teachers project will involve an international research experience where a high school chemistry teacher in Cincinnati will travel to Moscow to work in the lab of Nifant'ev assisting the graduate student and REU student on anionic polymerization of model branched polymers. The research is aimed at understanding the nature of and predicting the physical properties of branched molecular microstructures.

In Moscow Prof. Nifant'ev has strong working contacts with two Pedagogical Institutions for training of High School Teachers:

The Moscow State Pedagogical University (http://www.mpgu.ru): This is the main Pedagogical University of Russia and,

- The Moscow City Teachers' Training University (http://www.mgpu.ru): This is a mostly Moscow based University.

Both Universities have Departments of Chemistry where they prepare the future teachers of Chemistry. Prof. Nifant'ev's colleague, Dr. Dmitrii M.Roitershtein, works in The Moscow City Teachers' Training University as a head of the Organic Chemistry Division. His area of scientific expertise is the chemistry of lanthanides. At the moment they collaborate with him in preparing of new Nd-catalysts for the polymerization of dienes. Any contacts with Dr. Dmitrii M.Roitershtein within our project are possible, including contribution of his students in our research work. It is planned that the High School Teacher will interact with these teachers colleges either formally or informally in meetings to discuss possible long term relationships. At this stage the interaction with the Teachers Colleges are informal and may involve setting up collaborative teaching interactions with the teacher's Cincinnati High School over the Internet. It may also be useful for the high school teacher to discuss and compare teaching practices with his Russian counterparts. Housing for the teacher will be arranged by Prof. Nifant'ev and the post-doctoral researcher in Moscow. The stay in Moscow will take place in the summer and will last for about one month. A different high school chemistry teacher will be involved each year of the project. The teachers will attend Russian language classes with other foreign researchers in the Chemistry College of Moscow State University during the stay.

2) Nature of Teacher Activities.

The high school teacher will travel to Moscow State University in Russia and will live in a premium dorm at the university for one month. He will participate with the undergraduate student, graduate student and post-doctoral researcher in the synthesis of monodisperse model polymers. These polymers will be used to understand the affect of polydispersity in molecular weight and topology on the various characterization techniques implemented for the main catalyst development project. The high school teacher will also interact with Prof. Nifant'ev's group as well as the group of Prof. Beaucage and will participate in weekly web-based videoconference concerning the project. Depending on the expertise of the high school teacher he/she will be allowed to participate in the design of new synthesis procedures and the types of chain microstructure that will be constructed.

The high school teacher will develop a web page and polymer synthesis teaching module for his high school class using atom transfer radical polymerization (ATRP) of polyacrylamide which is a living polymerization that parallels anionic polymerization but with mild reagents and being less sensitive to water and oxygen. In Moscow he will produce polymers using ATRP that parallel in polydispersity and molecular weights the polymers being produced for the chain microstructure study. The teaching module will discuss the properties of polymers that are affected by chain topology. The teacher will perform characterization of his ATRP polymers at Moscow State University and will use this information in his teaching module.

2) Experience of the Principal Investigator

Prof. Beaucage has previously worked with a minority high school teacher from Princeton High School in Cincinnati, Edwin Segbefia, Figure 1. Segbefia worked two summers on a project involving synthesis of nanoparticles in flames. He interacted closely with two REU students, Stephanie Berger and Robin Holland. Last summer Segbefia worked with these REU students on several projects including synthesis of carbon coated titania and studies of maghemite synthesis in spray flames conducted in our spray flame pyrolysis setup, Fig. 1b, as well as in a simple oil lamp using ethanol and ferrocene which are inexpensive and available through Aldrich and Sigma suppliers, Fig. 2. We have developed a web based teaching module that demonstrates the use of these simple diffusion flames to produce nano-particles that are magnetic. Students form Princeton high school visited UC to observe electron microscopy of the particles they produced in their high school laboratories using this module. The teaching module is posted on the PI's web page (http://www.eng.uc.edu/~gbeaucag/Classes/Ferrocene Burner.html). Evaluation of the teaching module by the high school students and Segbefia was planned. A web-based evaluation was also linked at the web page.

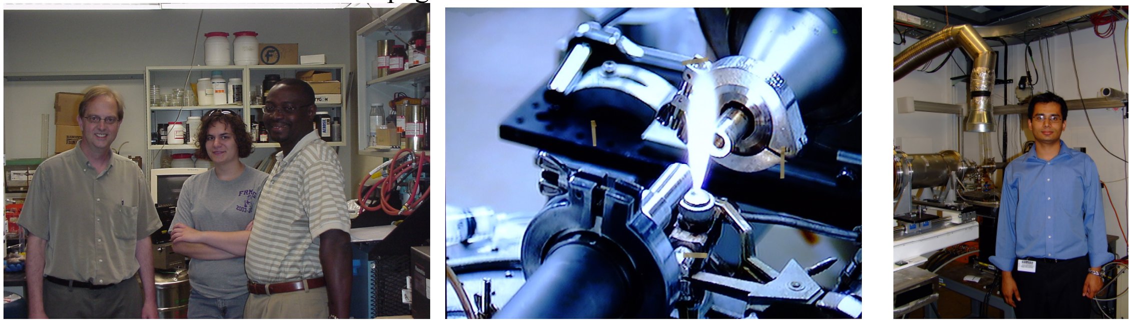


Figure 1. a) Greg Beaucage, Stephanie Berger (REU Student), Edwin Segbefia (RET Teacher), b) Spray flame for supported gold catalysts. c) Graduate student Sachit Chopra with flame spray pyrolysis setup at the Advanced Photon Source, Argonne National Laboratories.

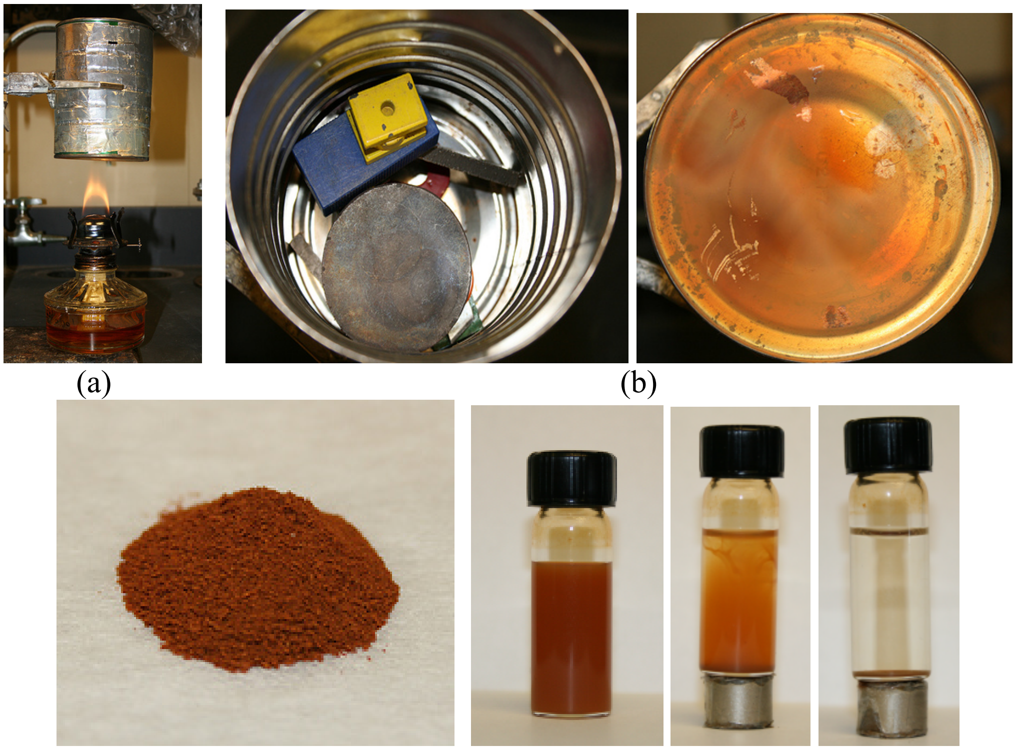
Additionally, Edwin and Stephanie and Robin were able to go on two experimental trips to the National Institute of Standards in Gaithersburg Maryland where they assisted in neutron scattering measurements with the PI and a graduate student. Edwin and Stephanie also traveled to Argonne National Laboratories Advanced Photon Source (APS) were we performed in situ x-ray scattering (SAXS) measurements on nano-particles during formation in spray and diffusion flames. Edwin was able to perform in situ SAXS measurements on his oil lamp setup. This data was incorporated in the web-teaching module. It is hoped that the interaction with Edwin will enable high school students from Princeton High School to travel to one of these national user facilities in the future to participate in these measurements though funding for this has not yet been obtained.

Stephanie and the graduate student Sachit Chopra, Figure 1, participated in an International Research and Education in Engineering (IREE) Project on spray flames where they stay in Zurich Switzerland for 6 months studying reactivity of gold catalysts produced in spray flames. This project is in collaboration with Sotiris Pratsinis and Jeroen van Bokhoven at ETH. Work at the European Synchrotron Research Facility in Grenoble France using SAXS was also conducted during this IREE Project and coincided with a trip by the REU student to Switzerland in the summer.

The PI has also taught at an NSF funded high school teacher-training program at Miami University in Oxford Ohio (taught at the Middletown campus) for several summers. The focus of this program was the development and dissemination of laboratory exercises to high school teachers for use in their home institutions. Teachers traveled from across the US to attend classes and labs. The course was free and teachers were provided travel funds to attend. The PI has also had an underprivileged minority high school student as a summer intern for one summer.

3) Participant Recruitment:

The previous RET participant was found by calling a number of local high schools and requesting for those interested. Edwin Segbefia had an unusually strong resume in that he had previously earned a research MS degree in Physics and had done some worked towards a PhD. He had already worked at a small synchrotron and had good lab and technical writing skills. It is unlikely that a similarly trained high school teacher will be found for this project, but a suitable candidate will be found in a similar manner, that is, by canvassing local high schools in a widening perimeter from the University until a reasonable candidate is found. Preference will be given to women and minorities.


(a) (b)

(c) (d)

Figure 2. a) Simple oil lamp burner with ethanol/ferrocene solution as fuel for high school teaching module. b) Thermophoretic and magnetic collection of nanoparticles using a coffee can filled with cold water and magnets for high school teaching module. c) Hematite nanopowder from flame spray pyrolysis (figure 1b) at UC. d) Magnetic separation of hematite nanoparticles from water at UC as a route to heavy metal remediation from drinking water.

4) Transfer of new knowledge to classroom activities & Follow up Plan.

There will be three main mechanisms for transfer of the RET results to the high school classroom. a) Development of a web page teaching module for ATRP polymerization of polyacrylamide in a high school chemistry lab. b) Web based interaction between Cincinnati high school class and Moscow State University Teaching College. c) Visit of high school students to the University of Cincinnati to characterize polymers made in the high school lab using NMR and IR spectroscopy.

5) Project Evaluation Reporting:

The project will be evaluated by the High School teacher with an assessment at the state to indicate expectations and at the end of the project to assess the impact of the project on the teachers capabilities. One year after the project the teacher will be asked to critique the program to assess the impact on teaching at the High School as well as exposure of the students to international research in Chemistry. The students who participate in the web based teaching module, interaction with Russian chemists and the visit to the University of Cincinnati will be surveyed as to the value of the program.

Request for an REU Supplement (3 pages)

A Research Experience for Undergraduates (REU) supplement is requested for the project "International Collaboration in Chemistry: *New polyolefin architectures via advanced catalysts and customized chain control agents*" that will allow a US citizen or permanent resident undergraduate engineering student to participate in this research project.

1) Overview: Description of the REU activity.

The proposed research experience for undergraduates project will involve an international research experience where an undergraduate Chemistry or Chemical Materials Engineering student will travel to Moscow to work in the lab of Nifant'ev assisting the graduate student and RET teacher on anionic polymerization of model branched polymers. The research is aimed at understanding the nature of and predicting the physical properties of branched molecular microstructures. Housing for the undergraduate will be arranged by Prof. Nifant'ev and a post-doctoral researcher in Moscow. The trip will take place in the summer and will last for 10 weeks. A different undergraduate will be involved each year of the project. The undergraduate student will attend Russian language classes in the College of Chemistry at Moscow State University with other foreign researchers.

2) Nature of Student Activities.

The undergraduate will travel to Moscow State University in Russia and will live in a dorm at the university for 10 weeks. He/She will participate with the high school teacher, graduate student and post-doctoral researcher in the synthesis of monodisperse model polymers. These polymers will be used to understand the affect of polydispersity in molecular weight and topology on the various characterization techniques implemented for the main catalyst development project. The undergraduate will also interact with Prof. Nifant'ev's group as well as the group of Prof. Beaucage and will participate in weekly web-based videoconference concerning the project.

The student will assist the high school teacher in the development of a web page and polymer synthesis teaching module for his high school class using atom transfer radical polymerization (ATRP) of polyacrylamide which is a living polymerization that parallels anionic polymerization but with mild reagents and being less sensitive to water and oxygen. In Moscow he/she will produce polymers using ATRP that parallel in polydispersity and molecular weights the polymers being produced for the chain microstructure study. The teaching module will discuss the properties of polymers that are affected by chain topology. The teacher will perform characterization of his ATRP polymers at Moscow State University and will use this information in his teaching module. The ATRP synthesis will be written up as an article for the Journal of Chemical Education by the undergraduate and high school teacher.

2) Experience of the Principal Investigator

Prof. Beaucage has previously worked with 3 REU students and a minority high school RET teacher from Princeton High School in Cincinnati, Edwin Segbefia, Figure 1. Segbefia worked two summers on a project involving synthesis of nanoparticles in flames. He interacted closely with two REU students, Stephanie Berger and Robin Holland. Segbefia worked with these REU students on several projects including synthesis of carbon coated titania and studies of maghemite synthesis in spray flames conducted in our spray flame pyrolysis setup, Fig. 1b, as well as in a simple oil lamp using ethanol and ferrocene which are inexpensive and available through Aldrich and Sigma suppliers, Fig. 2. We have developed a web based teaching module that demonstrates the use of these simple diffusion flames to produce nano-particles that are magnetic. Students form Princeton high school visited UC to observe electron microscopy of the particles they produced in their high school laboratories using this module. The teaching module is posted on the PI's web page (http://www.eng.uc.edu/~gbeaucag/Classes/Ferrocene Burner.html). Evaluation of the teaching module by the high school students and Segbefia was planned. A web-based evaluation was also linked at the web page.

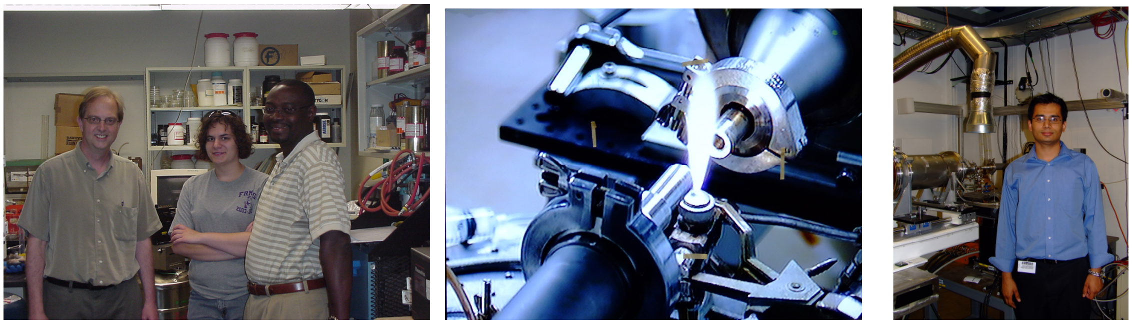
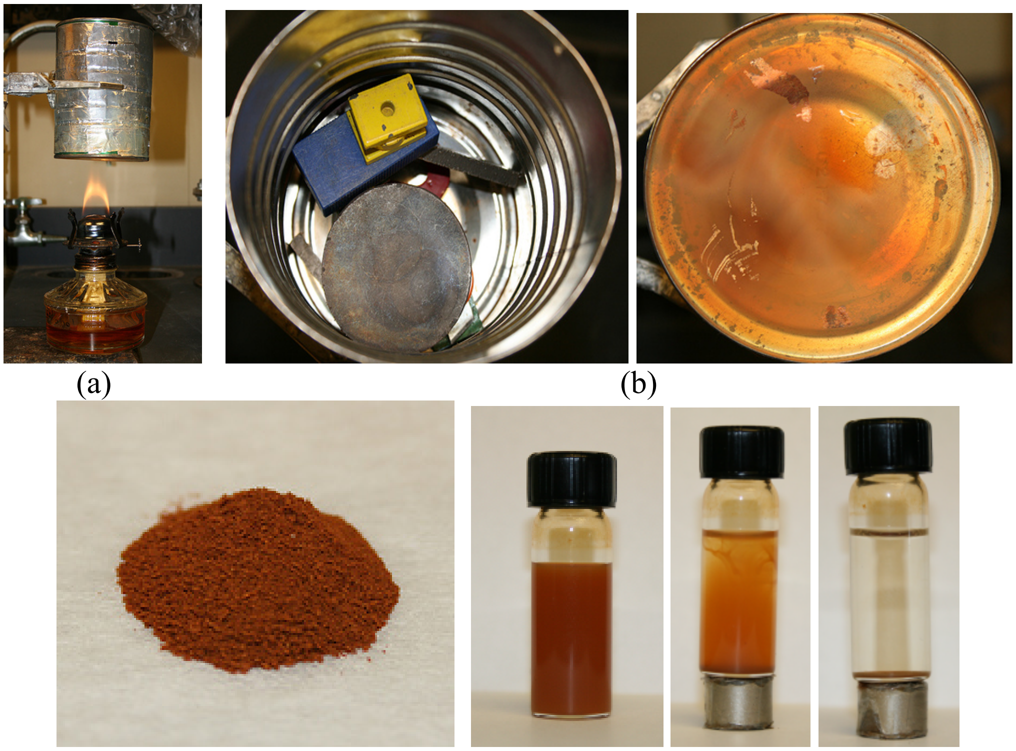


Figure 1. a) Greg Beaucage, Stephanie Berger (REU Student), Edwin Segbefia (RET Teacher), b) Spray flame for supported gold catalysts. c) Graduate student Sachit Chopra with flame spray pyrolysis setup at the Advanced Photon Source, Argonne National Laboratories.



(a) (b)

(c) (d)

Figure 2. a) Simple oil lamp burner with ethanol/ferrocene solution as fuel for high school teaching module. b) Thermophoretic and magnetic collection of nanoparticles using a coffee can filled with cold water and magnets for high school teaching module. c) Hematite nanopowder from flame spray pyrolysis (figure 1b) at UC. d) Magnetic separation of hematite nanoparticles from water at UC as a route to heavy metal remediation from drinking water.

Additionally, Edwin and Stephanie and Robin were able to go on two experimental trips to the National Institute of Standards in Gaithersburg Maryland where they assisted in neutron scattering measurements with the PI and a graduate student. Edwin and Stephanie also traveled to Argonne National Laboratories Advanced Photon Source (APS) were we performed in situ x-ray scattering (SAXS) measurements on nano-particles during formation in spray and diffusion flames. Edwin was able to perform in situ SAXS measurements on his oil lamp setup. This data was incorporated in the web-teaching module. It is hoped that the interaction with Edwin will enable high school students from Princeton High School to travel to one of these national user facilities in the future to participate in these measurements though funding for this has not yet been obtained.

Stephanie and the graduate student Sachit Chopra, Figure 1, participated in an International Research and Education in Engineering (IREE) Project on spray flames where they stay in Zurich Switzerland for 6 months studying reactivity of gold catalysts produced in spray flames. This project is in collaboration with Sotiris Pratsinis and Jeroen van Bokhoven at ETH. Work at the European Synchrotron Research Facility in Grenoble France using SAXS was also conducted during this IREE Project and coincided with a trip by the REU student to Switzerland in the summer.

The PI has also taught at an NSF funded high school teacher-training program at Miami University in Oxford Ohio (taught at the Middletown campus) for several summers. The focus of this program was the development and dissemination of laboratory exercises to high school teachers for use in their home institutions. Teachers traveled from across the US to attend classes and labs. The course was free and teachers were provided travel funds to attend. The PI has also had an underprivileged minority high school student as a summer intern for one summer.

3) Participant Recruitment:

Undergraduates will be recruited via an advertisement placed on the PI's web page and the PI will place fliers around campus indicating that this research position is open for the summer. Announcements will also be made in classes taught by the PI. In the past it has not proven difficult to locate undergraduate students interested in this work. The main criterion will be for a student interested in pursuing graduate education who has interest in chemical synthesis and catalysis and some inclination towards experimental work. It will be attempted to locate a student with some knowledge of Russian. Other criteria will be for female and minority students and students with a background suitable for a graduate program in Chemical or Materials Engineering. All 3 of the REU students Prof. Beaucage has had were women and one a minority. Beaucage has also had a number of minority and women students work on senior projects.

4) Transfer of new knowledge to classroom activities & Follow up Plan.

The REU project will be assessed by an exit survey of the undergraduate and by the delivery of a manuscript for the research work. The manuscript will pertain to an article for the Journal of Chemical Education focusing on ATRP polymerization and polymer chain microstructure. It is expected that the undergraduate will present the summer work at the American Chemical Society National Meeting in August. This meeting trip will be funded by funds available for undergraduate researchers at the University of Cincinnati.

lyondellbasell

Sandor Nagy, Ph.D.
LyondellBasell Industries
11530 Northlake Drive
Cincinnati, OH 45249
Phone: 513.530.4220

January 28, 2010

Dear Sir or Madam,

I intend to collaborate as a non-funded participant in the project, "*New polyolefin architectures via advanced catalysts and customized chain control agents*", being submitted by Prof.. Greg Beaucage at the University of Cincinnati. We hope to work with Beaucage in the development of exciting new approaches toward polyolefins with unique macrostructures.

I plan to spend a considerable amount of my time (up to 8 hours per week, depending on project needs) on developing computational based approaches toward rational design of new catalytic systems supporting this project, as well as supervise polymerization procedures to prepare polymer samples for Prof. Beaucage's structural studies.

Sincerely,

Sandor Nagy, Ph.D.

Equistar Chemicals, LP
11530 Northlake Drive
Cincinnati, OH 45249
Ph. 1.513.530.4000

Fax. 1.513.530.4268
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A Lyondell Company

Sandor M. Nagy

Senior Research Scientist
Equistar Chemicals, a LyondellBasell Industries Company
Cincinnati Technology Center
e-mail: sandor.nagy@lyondellbasell.com

Cincinnati Office:	Morris Office:	Home:
11530 Northlake Dr.	8805 North Tabler Rd.	516 Stanhope Ct.
Cincinnati, OH 45249	Morris, IL 60450	Naperville, IL 60565
Phone: 513-530-4220	Phone: 815-942-7421	Phone: 630-848-0180
	Fax: 815-942-7422	

Education

1979 St.Petersburg (Leningrad) University, St.Petersburg, Russia; ***M.S. Organic Chemistry***: Advisor A.P.Molchanov. *Reactivity of Unsaturated Carbenes*.
1985 Novosibirsk Institute of Organic Chemistry, Russian Academy of Sciences, Novosibirsk, Russia; ***Ph.D. Physical Organic Chemistry***: Advisor G.I.Borodkin. *Rearrangement of Carbonium Ions in Crystalline State.*

Employment

Equistar Chemicals, a LyondellBasell Industries Company, Cincinnati, OH. ***Senior Research Scientist***, Catalyst Group, 1998-present.
Occidental Chemical Co., Grand Island, NY. ***Research Scientist***, Research and Technology Center, 1992-1998.
Novosibirsk Institute of Organic Chemistry, Russian Academy of Sciences, Novosibirsk, Russia. ***Research Associate***, Laboratory of Mechanisms of Organic Reactions. 1979-1992.

Other Experience and Memberships

1992-present American Chemical Society
1989-1992 Lecturer at Novosibirsk State University (Organic Chemistry)

Research Interests

Mechanisms of catalytic processes; rational design of complex chemical systems; industrial catalytic processes; applied computational chemistry.

Patents (last 5 years) – from 74 allowed US Patents, more than 10 pending applications.

US 7,638,584 (2009) Nagy, S.; Tsuie B.M.; Clemons R.J. - *Olefin polymerization process*
US 7,473,745 (2009) Chandrashekar, V.; Mack M.P.; Gates C.H.; Holland, C.S.; Nagy, N., Nagy, S.; Vargas, E.S., Merrick-Mack, J.A. – *Preparation of multimodal polyethylene*
US 7,189,675 (2007) Nagy, S – *Olefin polymerization catalyst on plasma-contacted support*
US 7,144,964 (2006) Nagy, S.; Mack, M.P. – *Solution polymerization process utilizing preassembled bimetallic Ziegler-Natta catalysts*
US 7,122,497 (2006) Nagy, S.; Tsuie, B. – *Olefin polymerization catalyst system*
US 7,091,291 (2006) Nagy, S. – *Olefin polymerization process*
US 7,078,362 (2006) Nagy, S. – *Carbene donor modified Ziegler Natta catalysts*
US 7,049,262 (2006) Nagy, S.; Johnson, K.W. – *Cryogenic method for forming supported catalysts*
US 7,026,415 (2006) Nagy, S.; Tsuie, B.M. – *Clatrochelates as olefin polymerization catalyst components*
US 7,005,489 (2006) Nagy, S.; Mack, M.P. – *Zwitterionic metallacycles*
US 6,998,451 (2006) Nagy, S.; Neal-Hawkins, K. – *Olefin polymerization process*
US 6,995,216 (2006) Winslow, L.N. – *Process for manufacturing single-site polyolefins*

US 6,984,499 (2006) Nagy, S. – *Olefin polymerization catalysts based on hydroxyldepleted calicarene ligands*
US 6,982,305 (2006) Nagy, S. – *Olefin polymerization in the presence of a dehydrogenation catalyst*
US 6,958,377 (2006) Nagy, S. – *Olefin polymerization process*
US 6,933,354 (2005) Lynch, M.W.; Meverden, C.C.; Nagy, S.; Neal-Hawkins, K.L. – *Aluminoboronate activators for single-site olefin polymerization catalysts*
US 6,908,972 (2005) Tsuie, B.M.; Neal-Hawkins, K.L.; Nagy, S.; Lynch, M.W.; Mack; M.P.; Wang, S.; Merrick-Mack, J.A.; Lee, C.A.; Mutchler, J.A.; Johnson, K.W. – *Method for making polyolefins*
US 6,884,749 (2005) Neal-Hawkins, K.L.; Nagy S.M.; Sartain, W.J.; Gupte, K.; Johnson, K.W. – *Supported catalysts which reduce sheeting in olefin polymerization*
US 6,875,829 (2005) Nagy, S. – *Single-site catalysts containing chelating N-oxide ligands*
US 6,841,500 (2005) Nagy, S.; Tsuie, B.M.; Sartain, W.J. – *Bimetallic indenoindolyl catalysts*
US 6,838,410 (2005) Wang, S.; Lee, C.C.; Mack, M.P.; Hlatky, G.G.; Nagy, S.; Tsuie, B.M.; Meverden, C.C. – *Catalysts for making polyolefins*

Selected Research Papers – from 15 peer reviewed publications

Modeling and catalytic performance of group 4 metal complexes with anionic heteroatomic ligands **-** Nagy, Sandor M.; Mack, Mark P.; Hlatky, Gregory G.; ACS Symposium Series (2003), 857(Beyond Metallocenes), 76-85.
Intramolecular borylation reaction catalyzed by Lewis acid: preparation of 1H-2,1-benzazaborole derivatives - Genaev, Alexander M.; Salnikov, Georgii E.; Shubin, Vyacheslav G.; Nagy, Sandor M.; Chemical Communications (Cambridge) (2000), (17), 1587-1588.
Silica-supported zirconocene catalysts: Preparation, characterization and activity in ethylene polymerization **-** Moroz, Boris L.; Semikolenova, Nina V.; Nosov, Andrey V.; Zakharov, Vladimir A.; Nagy, Sandor; O'Reilly, Neil J.; Journal of Molecular Catalysis A: Chemical (1998), 130(1-2), 121-129.
Selectivity of nitration reactions of aromatic compounds on zeolites H-Y and H-ZSM-11 **-** Nagy, Sandor M.; Yarovoy, Konstantin A.; Shubin, Vyacheslav G.; Vostrikova, Lidiya A. - Journal of Physical Organic Chemistry (1994), 7(7), 385-93.
On the nature of zeolite catalyst effect on the selectivity of toluene nitration by acyl nitrates. Nagy, S. M.; Yarovoy, K. A.; Vostrikova, L. A.; Ione, K. G.; Shubin, V. G. - Studies in Surface Science and Catalysis (1993), 75(New Frontiers in Catalysis, Pt. B), 1669-72.
Nitration of aromatic compounds with benzoyl nitrate on zeolites - Nagy, S. M.; Yarovoi, K. A.; Shakirov, M. M.; Shubin, V. G.; Vostrikova, L. A.; Ione, K. G.; Journal of Molecular Catalysis (1991), 64(3), L31-L34.
Carbonium ion rearrangement in the crystalline state: isokinetic phase point - Borodkin, G. I.; Nagy, S. M.; Mamatyuk, V. I.; Shakirov, M. M.; Shubin, V. G.; Journal of the Chemical Society, Chemical Communications (1983), (24), 1533-5.

Collaborators (Last 5 Years)

Prof. I.E.Nifant'ev	Moscow State University, Russia; *Development of post-metallocene catalysts*;
Dr. S.Mihan	Basell GmbH, Frankfurt, Germany; *Development of polymerization catalysts*;
Dr. G.Morini	Basell Poliolefine Italia S.r.l., Ferrara, Italy; *Development of Ziegler-Natta systems*;
Prof. V.G.Shubin	Novosibirsk Institute or Organic Chemistry, Russian Academy of Sciences, Novosibirsk, Russia; *Development of new ligands;*
Prof. J.M.Caruthers	Purdue University, School of Chemical Engineering; West Lafayette, IN; *Modeling of complex chemical systems.*

VASSILIOS GALIATSATOS, PhD
Fellow of the Society of Plastics Engineers

EDUCATION

1986	Ph.D. in Polymer Science (Div. of Physical Chemistry) THE UNIVERSITY OF CINCINNATI, Cincinnati, OH. Advisor: J.E. Mark
1986	Masters of Science Degree in Chemistry THE UNIVERSITY OF CINCINNATI, Cincinnati, OH. Advisor: J.E. Mark
1982	Bachelor of Science Degree in Chemistry THE UNIVERSITY OF THESSALONIKI - GREECE.

PROFESSIONAL EXPERIENCE

2001 to present	Consulting Researcher – LyondellBasell Industries Cincinnati, OH
2000 to 2001	Staff Scientist – Abbott Labs Ashland, OH
1996 to 2000	Staff Scientist – Huntsman Polymers Corp. Odessa, TX
1990 to 1996	Assistant Professor - Polymer Science The University of Akron, Akron, OH
1988 to 1990	Senior Research Physicist Goodyear Tire and Rubber Co., Akron, OH
1986 to 1988	Postdoctoral Research Associate - Chemistry The University of Washington, Seattle, WA
1982 to 1986	Research Assistant - Chemistry The University of Cincinnati, Cincinnati, OH.

PROFESSIONAL AWARDS AND HONORS

2007 Appointed Vice-President and Member of the Executive Committee – Society of Plastics Engineers
2007 International Councilor Service Award – Society of Plastics Engineers
2007 Elected General Operating Chair for ANTEC07 Conference – Society of Plastics Engineers
2006 Recipient of Sparks-Thomas Award for innovation in research – Rubber Division – American Chemical Society
2004 International Councilor Service Award – Society of Plastics Engineers
2004 Elected Technical Program Chair for ANTEC04 Conference
2001 Elected as a Fellow Member of the Society of Plastics Engineers
1999 Division Chairman - Polymer Analysis Division, Society of Plastics Engineers
1996 Outstanding Service Award - Polymer Analysis Division, Society of Plastics Engineers
1995 Induction by the University of Akron into the American Society of Patent Holders as a Distinguished Corporate Inventor
1995 Outstanding Service Award - Polymer Analysis Division, Society of Plastics

Engineers
1990 Academic Challenge III Award Faculty position - Ohio Board of Regents

SERVICE TO THE PROFESSION

1994 to 1997	Review panel member for NIH Research (1994: NIDR Centers of Excellence; 1995: SBIR Phase I)
1994 to present	Board of Directors - International Polymer Networks Group
1991 to present	Board of Directors – Polymer Analysis Division, Society of Plastics Engineers
1990 to 1996	Editorial Board, *Chemical Design and Automation*
1987 to present	Reviewer for Macromolecules, Journal of Polymer Science - Physics, Polymer (London), Rubber Chemistry and Technology, Journal of the American Chemical Society, European Polymer Journal, Journal of Computational Polymer Science
	Reviewer for National Science Foundation, National Research Council, Petroleum Research Fund (ACS)

PATENTS

1994	**US PATENT 5,376,738** on molecular reinforcement of silicone elastomers
1995	**U.S. PATENT 5,676,972** on controlled release formulations of polymer gels
2003	**U.S. PATENT 6,599,987** on water-soluble, curable copolymers, methods of preparation and uses thereof

BUSINESS CONSULTING

1990 to 1996	Americhem - Akron, OH - on polymer characterization
	Bicron Corp. - Newbury, OH - on silicone rubber fundamentals
	Biosym Technologies Corp. - San Diego, CA - on polymer modeling
	Kumho Tire Co. - South Korea – on rubberlike elasticity
	Lord Corp. - Cary, NC – on polymer networks
	Owens Corning Fiberglas Corp. - Granville, OH – on polymer modeling
	Raychem Corp. - Menlo Park, CA – on polymer modeling

2 PUBLICATIONS OF 43

Galiatsatos, V., Editor "**Molecular Simulation Methods for Predicting Polymer Properties**" – Wiley Interscience - 2005

Galiatsatos, V. "**Optical Properties of Polymers**" – Encyclopedia of Polymer Science and Engineering – Wiley – 2003 (updated in 2006)

Dr. Marc Oliver Kristen
Lyondellbasell Industries
Basell Polyolefine GmbH
Catalyst Systems
Industriepark Höchst
Building E 413
65926 Frankfurt
Germany

10/1986 – 08/1992	Study of Chemistry at University of Bielefeld
09/1989 – 05/1990	Study at University of Michigan, Ann Arbor, USA
09/1992 – 02/1995	Research for doctoral thesis in Organometallic Chemistry at University of Bielefeld in the group of Prof. Jutzi
01/1994 – 04/1994	Research at University of North Carolina, Chapel Hill, USA in the group of Prof. Brookhart
02/1995	“Dr. rer. nat.” at University of Bielefeld.
03/1995 – 12/2001	BASF Aktiengesellschaft: Research chemist at Polymer Laboratory. Major fields of interest: Development of supported metallocene catalysts for polyethylene Catalytic emulsion polymerisation of polyolefins in water High throughput experimentation of polymerization catalysts
01/2002 – present	Basell Polyolefine GmbH: Head of High Throughput Experimentation: Responsible for entire Basell’s HTE activities

Author of more than 50 patents and patent applications. Referee for major chemical journals and the German Ministry of Education and Research. Mutiple invited oral presentations at major international conferences in the areas of organometallic chemistry, polymerization catalysis and high throughput experimentation.

Surname(s) / First name(s)	Fabrizio Piemontesi
Address(es)	Via Santa Margherita 92F, I-44100, FERRARA, Itly
Telephone(s)	Office + 39 532-467724
Nationality	Italian
Date of birth	6th April 1960
Gender	Male

Work experience:

October 2000 –

Occupation or position held: Responsible of Research Laboratory

Basic Research studies on heterogeneous Ziegler-Natta Catalysts (MgCl2 based). Cooperation in the development of new catalysts. Studies of 1-olefin homo and copolymerization with Heterogeneous ZN and Metallocene based catalysts

Name and address of employer: Basell Poliolefine Italia , “Giulio Natta” R&D Center; Piazzale Donegani 12 – Ferrara

April 1996 - October 2000

Occupation or position held: Responsible of Research Laboratory

Studies of homo and copolymerization of 1-olefin with metallocene based catalysts. Polymerization mechanisms Statistical modelling of homo and copolymerization

Name and address of employer Montell Italia, “Giulio Natta” R&D Center; Piazzale Donegani 12 – Ferrara Type of business or sectors

March 1989 - April 1996

Occupation or position held: Researcher

Synthesis and reactivity of Zirconium metallocenes for 1-olefin copolymerization

Himont “Guido Donegani” R&D Center Novara (up to December 1991) and “Giulio Natta” R&D Center; Piazzale Donegani 12 – Ferrara (from January 1992)

Education and training

October 1979 – October 1986 Title of qualification awarded: Italian Laurea in Chemistry

Organometallic Chemistry, Spectroscopy. Thesis on “Synthesis and characterization of metallic complexes of aminoacid Schiff’s basis” under the supervision of Prof. Luigi Casella

Università di Milano 109/110

Mother tongue(s) Italian

Other language(s) Self-assessment European level (*) English, French

Teaching experiences

Contract professor in University of Ferrara (3 years of a full year course in polymerization) and University of Padova (6-10 hours course during 6 years) Lecturer and Final Thesis Tutor in Master Course in cooperation with Universities of Ferrara and Rome

Organic and Organometallic Chemistry (University) 13C NMR of polyolefins (interaction and cooperation with internal NMR experts) Use of Markovian models for the study of homo and copolymerization reaction Setup of polymerization experiments Knowledge of the main structure-properties relationships in polyolefininic materials

Recent Publications

Co-author of about 41 papers

h-index = 9 (evaluated with “Harzing, A.W. (2009) Publish or Perish, version (2.8.3644), available at www.harzing.com/pop.ht”)

Key Elements in the Structure and Function Relationship of the $MgCl_2/TiCl_4$/Lewis Base Ziegler−Natta Catalytic System, Andrea Correa, Fabrizio Piemontesi, Giampiero Morini, and Luigi Cavallo Macromolecules, 2007, 40 (25), pp 9181–9189.

C1-symmetric heterocyclic zirconocenes as catalysts for propylene polymerization, 1: Ansa-zirconocenes with linked dithienocyclopentadienyl-substituted cyclopentadienyl ligands. Nifant'ev, Ilya E.; Laishevtsev, Ilya; Ivchenko, Pavel V.; Kashulin, Igor A.; Guidotti, Simona; Piemontesi, Fabrizio; Camurati, Isabella; Resconi, Luigi; Klusener, Peter A. A.; Rijsemus, Jos J. H.; de Kloe, Kees P.; Korndorffer, Frans M Macromolecular Chemistry and Physics 2004, 205(17), 2275-2291.

C2-symmetric zirconocenes for high molecular weight amorphous poly(propylene). Balboni, Davide; Moscardi, Gilberto; Baruzzi, Giovanni; Braga, Vittorio; Camurati, Isabella; Piemontesi, Fabrizio; Resconi, Luigi; Nifant'ev, Ilya E.; Venditto, Vincenzo; Antinucci, Simona. Macromolecular Chemistry and Physics 2001, 202(10), 2010-2028.

Selectivity in Propene Polymerization with Metallocene Catalysts. Resconi, Luigi; Cavallo, Luigi; Fait, Anna; Piemontesi, Fabrizio. Chemical Reviews (Washington, D. C.) 2000, 100(4), 1253-1345.

A New Class of Isospecific, Highly Regiospecific Zirconocene Catalysts for the Polymerization of Propene. Resconi, Luigi; Piemontesi, Fabrizio; Camurati, Isabella; Sudmeijer, Olof; Nifant'ev, Ilya E.; Ivchenko, Pavel V.; Kuz'mina, Lyudmila G. Journal of the American Chemical Society 1998, 120(10), 2308-2321.

Recent Patents

Co-inventor of about 25 patents in the field of metallocenes and Ziegler Natta catalytic systems for the synthesis of polyolefins,

- US2009326156 (A1) - 2009-12-31 Process for the preparation of a catalyst component and components therefrom obtained
- US2007021295 (A1) - 2007-01-25 Butene-1 (Co)Polymers Having Low Isotacticity - US2008004409 (A1) - 2008-01-03

The project "International Collaboration in Chemistry: *New polyolefin architectures via advanced catalysts and customized chain control agents*" will involve significant interaction with LyondellBasell Industries. A draft research agreement is included as a supplement in keeping with requirements in other NSF industry/academic collaborative programs such as the GOALI program. If the project is funded a signed research agreement will be negotiated prior to NSF funding to ensure protection of intellectual property and to allow open scientific discourse between the industrial and academic scientists involved in the work. *This draft agreement was written by Prof. Beaucage and is currently under consideration and significant modification by the legal counsel of LyondellBasell Industries.*

DRAFT INDUSTRIAL RESEARCH AGREEMENT

THIS RESEARCH AGREEMENT made and effective as of the date of last signing (herein the "Effective Date") by and between **LYONDELLBASELL INDUSTRIES,** 1221 McKinney Street, Suite 700, Houston, Texas 77010 on behalf of its subsidiary **Equistar Chemicals LP**, (herein "Sponsor"), a for-profit corporation, and the **UNIVERSITY OF CINCINNATI**, a state institution of higher education organized under Section 3361 of the Ohio Revised Code, (herein "UC)" on behalf of the College of Engineering, Department of Chemical & Materials Engineering having an office at University Hall, Suite 530, 51 Goodman Drive, Cincinnati, Ohio 45221-0222.

WHEREAS, the research program contemplated by this Agreement is of mutual interest and benefit to UC and to the Participant, and will further the instructional and research objectives of UC in a manner consistent with its status as a nonprofit, tax-exempt, educational institution,

NOW, THEREFORE, the parties hereto agree as follows:

1. **STATEMENT OF WORK.** UC agrees to use its reasonable efforts to perform the research program (herein the "Research Program") as set forth in Exhibit A.

2. **PRINCIPAL INVESTIGATOR.** Gregory Beaucage, Ph.D. will supervise the research. If, for any reason, that person is unable to continue to serve as Principal Investigator, Participant and UC shall attempt to find a successor acceptable to both parties. If such a successor is not available, this Agreement shall be terminated as provided in Article 6.

3. **PERIOD OF PERFORMANCE.** The research shall be conducted during the period beginning on the 9/01/10 and ending on 8/31/13 (herein the "Termination Date") and will be subject to renewal only by mutual agreement of the parties.

4. **REIMBURSEMENT OF COSTS.** No costs are expected from this agreement.

6. **EARLY TERMINATION.**

   A. Should UC breach this Agreement or become unable to perform hereunder, Participant shall have the right to terminate this Agreement. Participant shall notify UC of its intention to do so, and termination shall become effective sixty (60) days thereafter if UC is unable to cure the breach or rectify the problem.

B. Either party may terminate this Agreement upon thirty (30) days written notice to the other party.

7. REPORTS AND CONFIDENTIAL INFORMATION

A. From time to time during the term of this Agreement, UC will provide Participant with written summaries of research progress. A final report will be provided at completion.

B. As used herein, "Confidential Information" shall mean information, know-how, samples, drawings or data, technical or non-technical, relating to the Research Program, that originates with either party, is disclosed or provided to the other and is clearly labeled as "Confidential". If disclosed orally, the Confidential Information shall be promptly reduced to written form and labeled as "Confidential". The recipient may use the originator's Confidential Information for purposes of this Agreement, but agrees neither to use for any other purpose nor to disclose or provide such Confidential Information to any third party at any time during the term of this Agreement or thereafter, except as follows:

1. To the extent that such Confidential Information was known to the recipient from sources other than the originator prior to its disclosure hereunder, and this is demonstrably documented in written records made by recipient prior to such disclosure; or

2. To the extent that such Confidential Information in fact is public knowledge prior to or after its disclosure, other than through acts or omissions attributable to the recipient; or

3. To the extent that such Confidential Information was disclosed or provided to the recipient by a third party who did not derive such information from the originator; or

4. To the extent required by law, if a request is received under the Ohio Open Records Act, UC shall notify Participant in advance of releasing any Confidential Information.

C. Each recipient specifically agrees not to export or re-export any information and/or technical data and/or products in violation of any applicable USA laws and/or regulations.

D. Each recipient will retain control of Confidential samples received hereunder and will not provide them to parties who are not bound by this Agreement.

8. PUBLICATIONS. UC reserves the right to publish the results of its research performed hereunder. Before publishing, however, UC agrees to submit copies of any manuscript proposed for publication to Participant at least Thirty (30) days in advance of the presentation or publication date, and if Participant does not ask to defer publication within Thirty (30) days after receipt of the manuscript so that patent applications may be filed, UC may proceed with publication. In the event Participant asks to defer publication, UC shall not publish or otherwise disclose to any third party any of the information contained in the manuscript until such time as a patent application has been filed or the expiration of Sixty (60) days after the date of submission of the manuscript to Participant, whichever occurs first.

9. INTELLECTUAL PROPERTY.

A. Subject to Section 3345.14 of the Ohio Revised Code, title to any discovery or invention conceived or first reduced to practice in the performance of the research program, herein "Project Invention," shall be assigned to UC if all of the inventors are UC employees; shall be assigned jointly to Participant and UC if the inventors include employees of both parties; and shall be assigned to Participant if all the inventors are employees of Participant.

B. If Participant asks UC to file patent applications on a Project Invention, Participant agrees to pay the costs of filing, prosecution and maintenance of the resulting patent application(s) and patents maturing therefrom. Participant shall notify UC of those foreign countries in which it desires a license, in sufficient time for UC to satisfy the patent law requirements of that country.

C. If UC asks Participant to pay for the filing, prosecution or maintenance of a patent application or patent on a UC Project Invention, and Participant refuses, Participant's option rights with respect to such patent application or patent shall terminate immediately.

D. In consideration for research support and patent expenses received hereunder, UC grants to Participant an option (herein "the Option") to acquire a license to any UC Project Invention, including any patent applications and patents resulting therefrom, according to the terms and conditions set forth herein.

(1) The Option will expire on the Termination Date of this Agreement.

(2) Participant may exercise the Option by written notice to UC at any time prior to its expiration declaring Participant's intent to negotiate a license agreement with UC (herein the "License Agreement"). The parties shall begin to negotiate in good faith toward execution of the License Agreement under commercially reasonable terms within Sixty (60) days after receipt by UC of written notification by Participant.

(3) Participant agrees promptly to notify UC in writing at any time during the Option Period if Participant determines not to exercise the Option, and further agrees to provide UC in reasonable detail in writing the basis for such determination. The Option shall expire immediately on such notification.

E. Title to any copyrights or copyrightable material first produced in the performance of the Research Program shall remain with UC. UC shall grant to the Participant an irrevocable, royalty-free, non-transferable, non-exclusive right and license to use and reproduce all such copyrightable materials, including computer software and its documentation specified to be developed and delivered under the Statement of Work, for Participant's internal (non-commercial) purposes. UC further grants to Participant an option to negotiate a non-exclusive (or exclusive subject to third party rights, if any) royalty-bearing license to use, reproduce, display, distribute, and perform such computer software and its documentation for commercial purposes, such option to expire on the Termination Date. Computer software for which a patent application is filed shall be subject to paragraphs A-D above.

F. Tangible Research Property (herein"TRP") is defined for purposes of this Agreement as tangible (or corporeal) items produced in the course of research projects supported by UC or by external participants. TRP includes such items as: biological materials, engineering drawings, computer software, integrated circuit chips, computer databases, prototype devices, circuit diagrams, equipment. In the event that Subcontractor elects to establish property rights other than patents to any TRP developed during the course of the research, Subcontractor and UC will determine the disposition of rights to such property by separate agreement. UC will, at a minimum, reserve the right to use and distribute TRP for non-commercial research purposes.

G. All licenses granted pursuant to this Article 9 become effective as of the date the parties sign a subsequent license agreement.

10. USE OF NAMES. Neither party will use the name of the other in any advertising or other form of publicity without the written permission of the other.

11. ANIMAL AND HUMAN STUDIES. Any use of human subjects or live, vertebrate animals in the performance of research hereunder shall comply with all applicable laws and government regulations.

12. NOTICES. Any notices required to be given or which shall be given under this Agreement shall be in writing delivered by first class mail (air mail if not domestic) addressed to the parties as follows:

UNIVERSITY OF CINCINNATI

Deborah Galloway, Executive Director,
Sponsored Research Services
University Hall, Suite 530
51 Goodman Drive
University of Cincinnati
P.O. Box 210222
Cincinnati, Ohio 45221-0222

Phone: (513) 556-2873
Fax: (513) 556-4346
E-mail: Deborah.Galloway@uc.edu

SPONSOR

____
LYONDELL INDUSTRIES
Equistar Chemicals LP
Technology Center
11530 Northlake Drive
Cincinnati, OH 45249

Phone: ______
Fax: ______
E-mail: __________

In the event notices, statements, and payments required under this Agreement are sent by certified or registered mail by one party to the other party at its above address, they shall be deemed to have been given or made as of the date so mailed, otherwise as of the date received.

13. ASSIGNMENT. This Agreement shall be binding upon and shall inure to the benefit of the parties hereto and the successors to substantially the entire business and assets of the respective parties hereto. This Agreement shall not be assignable by either party without the prior written consent of the other party.

14. GOVERNING LAW. The validity and interpretation of this Agreement and the legal relation of the parties to it shall be governed by the laws of the State of Ohio and the United States.

15. **GOVERNING LANGUAGE.** In the event that a translation of this agreement is prepared and signed by the parties for the convenience of the participant, this English language version shall be the official version and shall govern if there is a conflict between the two.

16. **EXPORT CONTROLS.** It is understood that UC is subject to United States laws and regulations controlling the export of technical data, computer software, laboratory prototypes, and other commodities, and that its obligations hereunder are contingent on compliance with applicable U.S. export laws and regulations (including the Arms Export Control Act, as amended, and the Export Administration Act of 1979). The transfer of certain technical data and commodities may require a license from the cognizant agency of the United States Government and/or written assurances by the Participant that the Participant will not re-export data or commodities to certain foreign countries without prior approval of the cognizant government agency. While UC agrees to cooperate in securing any license which the cognizant agency deems necessary in connection with this Agreement, UC cannot guarantee that such licenses will be granted.

17. **FORCE MAJEURE.** UC shall not be responsible to the Participant for failure to perform any of the obligations imposed by this agreement, provided such failure shall be occasioned by fire, flood, explosion, lightning, windstorm, earthquake, subsidence of soil, failure or destruction, in whole or in part, of machinery or equipment or failure of supply of materials, discontinuity in the supply of power, governmental interference, civil commotion, riot, war, strikes, labor disturbance, transportation difficulties, labor shortage, or any cause beyond the reasonable control of UC.

18. **WARRANTY DISCLAIMER.** Nothing in this Agreement shall be construed as:

    A. A warranty or representation by UC as to the validity or scope of any patent.

    B. A warranty or representation that anything made, used, sold or otherwise disposed of under any license that may be granted upon exercise of the Option is or will be free from infringement of patents, copyrights and trademarks of third parties;

    C. An obligation to bring or prosecute actions or suits against third parties for infringement;
    D. Conferring rights to use in advertising, publicity or otherwise any trademark or the name of UC; or
    E. Granting by implication, estoppel or otherwise any licenses under patents of UC other than patent(s) identified herein, regardless whether such other patents are dominant or subordinate to any such patent(s).

    Except as expressly set forth in this Agreement, UC MAKES NO REPRESENTATIONS AND EXTENDS NO WARRANTIES OF ANY KIND, EITHER EXPRESS OR IMPLIED. THERE ARE NO EXPRESS OR IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, OR THAT THE USE OF THE LICENSED PRODUCT WILL NOT INFRINGE ANY PATENT, COPYRIGHT OR TRADEMARK OR OTHER RIGHTS.

19. **ENTIRE AGREEMENT.** Unless otherwise specified, this Agreement embodies the entire understanding between UC and the Participant for this project, and any prior or contemporaneous representations, either oral or written, are hereby superseded. No amendments or changes to this Agreement, including without limitation, changes in the statement of work, total cost, and period of performance, shall be effective unless made in writing and signed by authorized representatives of the parties.

By signature below of duplicate originals, Participant and UC hereby agree to this Sponsored Research

Agreement as of the Effective Date.

UNIVERSITY OF CINCINNATI	**LYONDELLBASELL INDUSTRIES** on behalf of its subsidiary **Equistar Chemicals LP**
By_________________________________	By___________________________
Title_______________________________	Title_________________________
Date_______________________________	Date_________________________
Tax ID No. 31-6000989	Tax ID No.: ____________________

Форма 35

35.1.1. Название проекта (на русском языке)
«Полиолефины с новой архитектурой: синтез с использованием современных передовых катализаторов и специальных агентов контроля роста цепи»

35.1.2. Название проекта (на английском языке)
“New polyolefin architectures via advanced catalysts and customized chain control agents”

35.2. Фундаментальная научная проблема, на решение которой направлен проект

Синтез и исследование полиолефинов

Полиолефины – пластики, прогресс в производстве и изучении которых сегодня переживает настоящий бум. Главными преимуществами полиолефинов является низкая цена исходных мономеров, таких как этилен, пропилен и бутен-1, а также широчайший спектр приложений этих полимеров. В настоящее время наиболее масштабными сферами применения полиолефинов являются производство пленок, труб, разнообразной тары и упаковки, деталей для автомобильной промышленности и даже медицинские материалы. Внедрение все новых и новых марок полиолефинов с особыми свойствами чрезвычайно востребовано обществом, благодаря чему в наше время объем производства полиолефинов превышает 100 млн. тонн в год и уверенно опережает суммарный объем производства всех других пластиков.

Последние десятилетия ознаменовались прогрессом в двух важных направлениях.

- Во-первых, были созданы суппортированные на хлориде магния многоцентровые катализаторы Циглера-Натта [1-3]. Адекватный подбор внутренних и внешних доноров для таких систем позволяет контролировать активность и стереоселективность катализаторов.
- Во-вторых, были открыты моноцентровые (single-site) высокопроизводительные катализаторы, которые позволяют получать разнообразные полиолефины (полиэтилены, полипропилены, полибутены и т.д.) с узким молекулярно-массовым распределением и уникальной микроструктурой. Сначала широкое распространение получили металлоценовые катализаторы, представляющие собой циклопентадиенильные комплексы, как правило, Ti, Zr и Hf [4]. В последние несколько лет интерес смещается с металлоценовых на постметаллоценовые катализаторы, которые в настоящее время представляют собой «еще не освоенную территорию» и, поэтому, притягивают внимание исследователей.

Оба типа катализаторов были коммерциализированы, но их применение имеет очевидные ограничения. Например, непонятно, в какой степени индивидуальный каталитический центр титан-магниевого катализатора Циглера-Натта может регулироваться введением донора или любой другой добавки? Также неясно, как регулировать способность моноцентровых катализаторов в внедрению тех или иных мономеров с образованием полимера с достаточно сложной архитектурой и необходимой молекулярной массой? *Таким образом, сегодня в химии полиолефинов наиболее остро стоит задача по разработке доступных и эффективных методов синтеза сложных супрамолекулярных полиолефиновых структур с контролируемым положением и стереохимией заместителей, а также поиска эффективных катализаторов, которые и позволяют осуществлять такой синтез.*

35.3. Конкретная фундаментальная задача в рамках проблемы, на решение которой направлен проект:

Синтез полиолефинов с определенной архитектурой и заданными свойствами, а также новые научные подходы к созданию технологий по их производству

Коммерческие полиолефины созданные на основе этиленовых и пропиленовых гомо- и сополимеров чрезвычайно разнообразны и универсальны благодаря тому, что они являются полукристаллическими веществами, то есть смесью аморфной и кристаллической фазы, включающей в свой состав нано-размерные кристаллиты (Рис 1) .

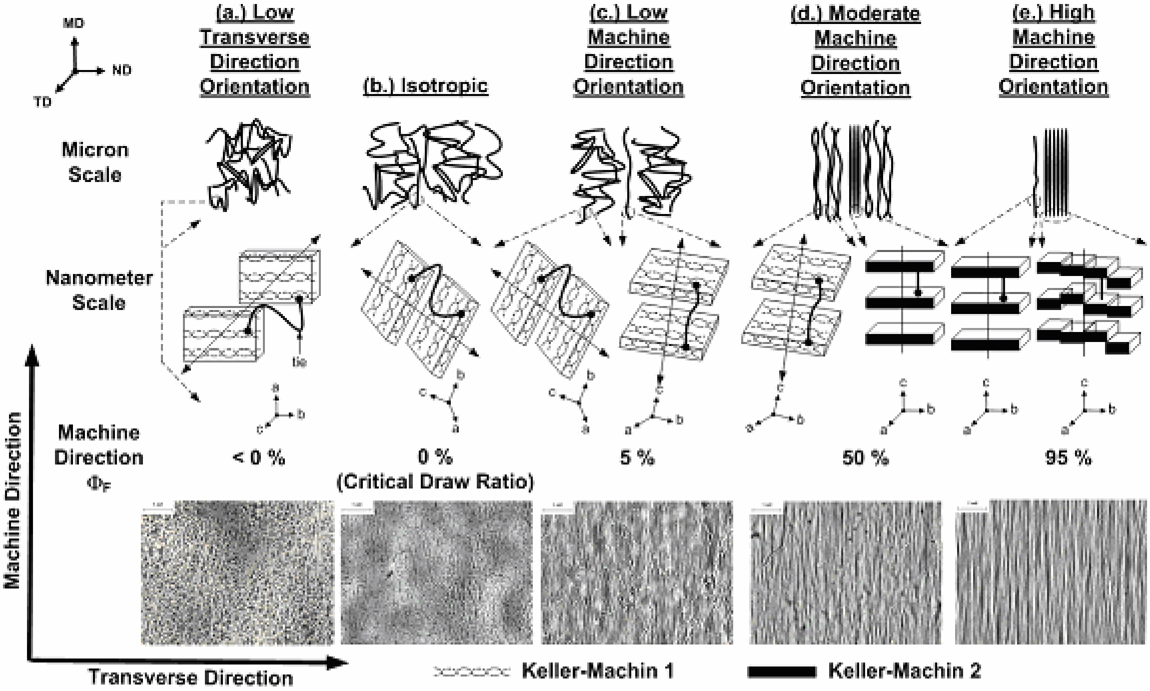

Рисунок 1. Схема изменения кристаллической структуры в микро- и наномаштабе во время кристаллизации из полиолефинного расплава под стрессомю. Наноструктурная динамика определяется структурой полимерной цепи. [5].

Начиная с открытия катализаторов Циглера-Натта, индустрия полиолефинов создала достаточно инструментов для контроля размера, формы и структуры полимеров, а также взаимосвязи этих параметров со структурой катализатора, условиями полимеризации. При этом, связь между кристаллической структурой и микроструктурой цепи была количественно описана, однако только недавно была изучена взаимосвязь кристаллической структуры, температуры плавления и топологии цепи, при этом использовались такие методы, как TREF (Temperature Rising Elution Fractionation) а также другие подходы [6,7].

Таким образом, дальнейший прогресс области полиолефинов обычно связывают с введением новых эффективных катализаторов, а также созданием полимеров с новой микроструктурой (молекулярный вес, молекулярно-массовое распределение, внедрение сомономеров, изоспецифическая полимеризация и т.д.), часто как раз благодаря использованию новых катализаторов [8-11].

Вместе с тем, синтез более продвинутых полимеров, содержащих супрамолекулярные фрагменты структуры, например, мультиблок-сополимеров с заданной структурой и контролируемым положением заместителей исходя из недорогих мономеров, является труднодостижимым. Цель данного проекта – разработать синтетические подходы к такого рода полимерам. В ходе настоящей работы для осуществления полимеризации будут применяться как новые катализаторы, так и специальные агенты контроля роста цепи. Помимо этого, мы разработаем специальные методы анализа новых полимеров и исследуем, их трехмерную структуру в твердом теле и в растворе.

35.4. Предлагаемые методы и подходы к решению поставленных задач

Успешное выполнение настоящего проекта потребует реализации следующих методов и подходов:

1. Разработка новых подходов к синтезу современных передовых полиолефиновых материалов с использованием оригинальных методов полимеризации, основанных на комбинации т.н. «живой» полимеризации и специальных агентов контроля роста цепи.
2. Разработка синтеза и получение полимеров с контролируемой молекулярной архитектурой путем направленного введения в полимер определенных заместителей. Особое внимание будет уделено осуществлению со-полимеризации этилена и пропилена с полярными со-мономерами, а также методам по установлению строения и свойств полученных полимеров.
3. Разработка оригинальных моноцентровых катализаторов полимеризации олефинов у которых способность к эффективной полимеризации олефинов будет сочетаться с низкой способностью к передаче цепи, что позволит получать полимеры с контролируемой молекулярной массой.
4. Разработка новых эффективных специальных агентов контроля роста цепи, совместимых с широким рядом функциональных групп. Эта область требует развития концептуально новых подходов и разработки доступных методов синтеза этих реагентов.
5. Разработка новых подходов к изучению и надежному установлению структуры новых материалов, установление комплексной взаимосвязи между структурой и свойствами новых материалов, а также исследование их возможной самосборки в твердой фазе и растворе.

Настоящий проект организационно задумывается не только как чисто академический. В случае поддержки в его реализации предполагается участие ***на безвозмездной основе*** специалистов LyondellBasell Industries (www.lyondellbasell.com) – мирового лидера в области технологии и производства полиолефинов. Такое сотрудничество позволит получить доступ к корпоративной информации и воспользоваться самой современной техникой и поддержкой со стороны признанного лидера отрасли. Например,

- проверку новых синтетических подходов предполагается осуществить в Научном центре LyondellBasell во Франкфурте, ФРГ (high-throughput testing lab) под руководством Dr. Marc Kirsten;
- исследование новых разветвленных полимеров на основе полипропилена и полибутена – в Научном центре LyondellBasell в Ферраре, Италия (G. Natta Research Center) под руководством Dr. Fabrizio Piemontezi;
- аналитическое исследование полученных полимеров, изучение характера разветвлений, а также моделирование новых катализаторов - в Научном центре LyondellBasell в Цинциннати, США под руководством Dr. Sandor Nagy и Dr. Vassilios Galiatsatos.

35.5. Согласованный с зарубежными партнерами детальный план научных исследований:

Настоящий проект решает две основные взаимосвязанные задачи:

Задача №1. Разработка катализаторов для получения полиолефина с контролируемой микроструктурой.

Задача №2. Синтез модельных разветвленных полимеров для опробования методик их исследования. Разработка новых методов исследования полимеров для количественного определения их химической микроструктуры и топологии.

Задача №1. Разработка катализаторов для получения полиолефина с контролируемой микроструктурой.

В течение последнего десятилетия смешанные моноцентровые катализаторы использовались для синтеза мультимодальных полимеров (Схема 1, Рис.2) либо высокоразветвленных полимеров с использованием индивидуальных или смешанных мономеров (Схема 2, Рис.3). В ходе интенсивного изучения некоторые системы были коммерциализованы с целью производства полиэтиленов с особыми свойствами.

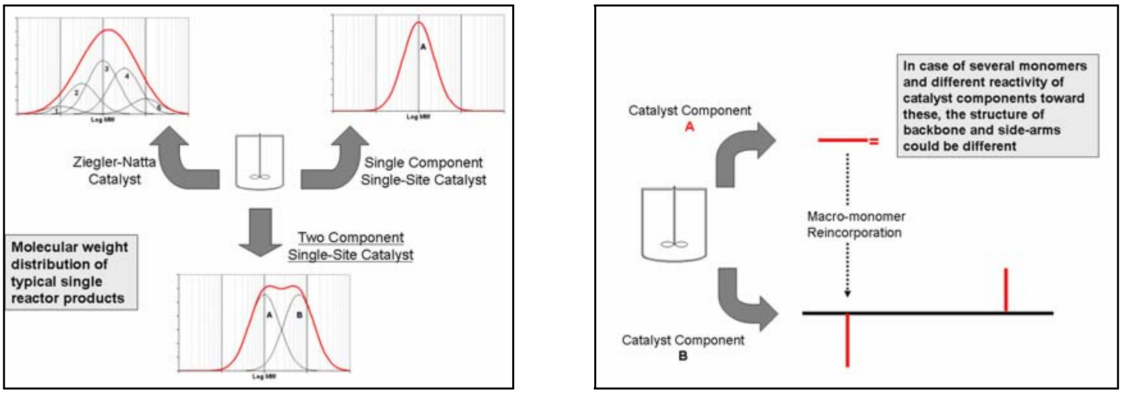

Схема 1 **Схема 2**

Рис.2 a) Схема 1, моноцентровые катализаторы для контролируемого синтеза мультимодального полимера; b) Схема 2, моноцентровые катализаторы для синтеза высокоразветвленного полимера

Недавние достижения в координационной полимеризации включают разработку контролируемого переноса цепи, с помощью которого потенциально можно получать ранее недоступные ди-блок и мульти-блок полиолефины (схемы 3 и 4, Рис.3) [8.9].

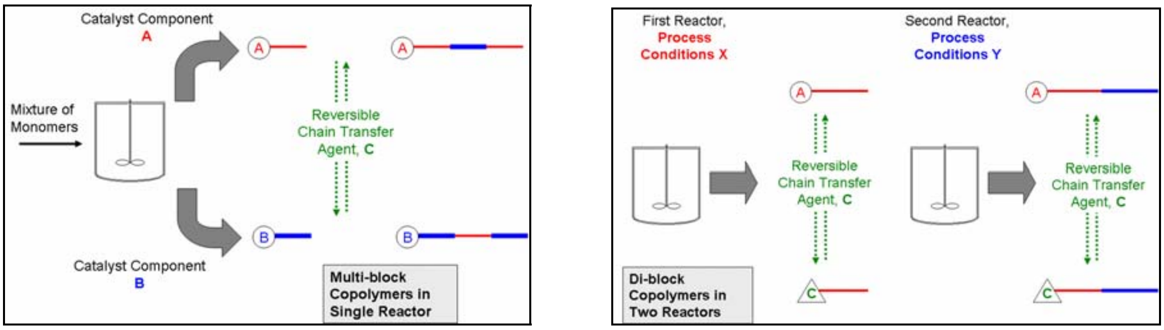

Схема 3 **Схема 4**

Рис.3. a) Схема 3, мультиблок сополимеры с использованием реагентов переноса цепи. b) Схема 4, диблок сополимеры с использованием двух реакторов и реагентов переноса цепи

Обычно, для осуществления синтезов, схематично изображенных на Схемах 1-4, используют постметаллоценовые моноцентровые катализаторы, которые демонстрируют подходящее соотношение в скоростях рост цепи/обрыв цепи, а также позволяют осуществлять полимеризацию олефинов с приемлемыми скоростями. Наиболее часто употребимые постметаллоценовые катализаторы, используемые с целью синтеза полиолефиновых блок-сополимеров приведены на Схеме 5 [9].

Scheme 5

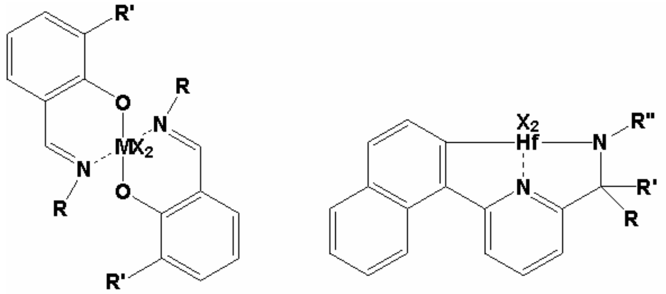

Рис.4. Пост-металлоценовые одноцентровые катализаторы, наиболее часто используемые для получения полиолефиновых блок-сополимеров [9].

Недавно мы обнаружили, что хинолиновый фрагмент является особенно многообещающим темплатом для конструирования на нем различных катализаторов полимеризации олефинов. Мы успешно разработали гибкий синтетический подход для получения хинолинов, функционализированных в положения 2- и 8- (Схема 6) и получили предварительные данные, позволяющие заключить, что хинолиновые комплексы различной топологии по своим каталитическим свойствам иногда превосходят все известные в настоящее время металлоценовые и пост-металлоценовые катализаторы [12-14].

Scheme 6

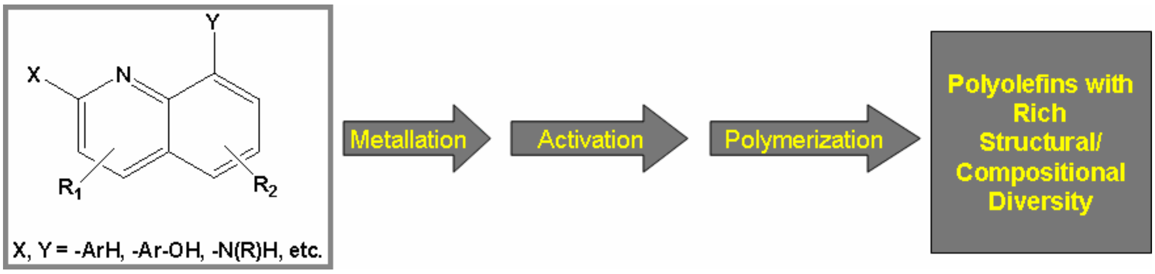

Схема 6, использование хинолина в качестве темплата для синтеза нового класса пост-металлоценовых катализаторов.

Активированные и протестированные в условиях применяемых в промышленности, новые катализаторы демонстрируют хорошую стабильность и высокую активность в полимеризации и сополимеризации этилена и пропилена. Предварительный анализ полиолефинов указывает на заметное влияние природы заместителя в положениях 2- и 8- на структуру получающегося полимера. Без сомнения, дальнейшее развитие хинолиновых катализаторов приведет к созданию уникальных каталитических систем, которые возможно будут востребованы промышленностью.

Одним из последних достижений в химии полиолефинов явилось открытие явления обратимого переноса цепи в ходе полимеризации (reversible chain-transfer agents), см. Схему 3, 4 [8-9]. Собственно, реальное применение нашел только один переносчик цепи – диэтилцинк. Другие цинкорганические соединения, будучи коммерчески недоступными, оказались неисследованными. В ходе реализации настоящего проекта предполагается получить и изучить широкий круг цинкорганических соединений в качестве переносчиков цепи. Кроме того, для этой цели будут также рассмотрены органические производные других непереходных металлов.

План работ в соответствие с Задачей №1

Первый год:

Синтез катализаторов: Приготовить хинолиновые комплексы различной структуры в соответствии реакционной последовательностью, изображенной на Схеме 6.

Переносчики цепи: синтезировать и исследовать ряд диалкил- и диарилцинков в качестве переносчиков цепи.

Компьютерное моделирование: Разработать модель для описания процесса переноса цепи диэтилцинком.

Использование высокопроизводительного тестирования катализаторов: Разработать надежную методику тестирования переносчиков цепи, используя литературные стандарты.

Второй год:

Синтез катализаторов: продолжение синтеза и исследования хинолиновых комплексов.

Переносчики цепи: исследовать производные непереходных металлов, отличных от цинка и алюминия в качестве переносчиков цепи.

Использование высокопроизводительного тестирования катализаторов: широкий скрининг различных пар катализатор/переносчик
Полимеризация в среднем масштабе: приготовить образец среднего масштаба (~100г), используя новые хинолиновые катализаторы.

Третий год:

Переносчики цепи: оптимизировать методику использования переносчиков цепи, показавших лучшие результаты в наших экспериментах.
Использование высокопроизводительного тестирования катализаторов: исследовать оптимальные условия осуществления полимеризации для отдельных пар катализатор/переносчик цепи.
Полимеризация в среднем масштабе: приготовить образец среднего масштаба (~100г) используя новые хинолиновые катализаторы и новый переносчик цепи.

Задача №2. Синтез модельных разветвленных полимеров для опробования методик их исследования.

Модельные полимеры для осуществления калибровки новых аналитических методов будут приготовлены с использованием методик, специально разработанных для этих целей. Так, полимеризацией бутадиена с использованием различных видов катализаторов будут получены полибутадиены различной архитектуры: линейный, гребнеобразный, «звездообразный» и др. Последующее гидрирование синтезированных полибутадиенов приведет к получению полиэтиленов различной архитектуры [15-19]. Используемые процедуры будут в дальнейшем применены для генерирования широкой библиотеки полимеров для использования в Московском Государственном Университете и в Университете Цинцинатти.

Экспреиментальное определение топологии разветвления модельных образцов и смесей с использованием SANS будет осуществлено в США на оборудовании расположенном в Oak Ridge и в NIST, а также на оборудовании, принадлежащем LyondellBasell в Цинцинатти. Корреляции, разработанные благодаря использованию экспериментов по рассеянию на модельных полимерах, будут использованы для характеризации материалов, приготовленных с использованием новых методов полимеризации, изучаемых в ходе выполнения Задачи №1.

План работ в соответствие с Задачей №2
Первый год:
- Синтез разветвленных полидиенов с различной архитектурой. Установление их строения;
- Гидрирование полученных разветвленных полидиенов.

Монодисперсный линейный полибутадиен будет синтезирован в первую очередь, затем будет получен «звездообразный» полимер.
- Начальные эксперименты по рассеянию нейтронов на полученных полимерах.

Второй год:
- Синтез гребнеобразных разветвленных полибутадиенов и их гидрирование с целью получения гребнеобразных полиэтиленов.
- Продолжение экспериментов по рассеянию нейтронов на полученных полимерах.

Третий год:
- завершение работ по синтезу полибутадиенов с различной архитектурой, получение Н-полимеров и их исследование методом рассеяния нейтронов.
- обобщение полученных результатов.

Научные работы, выполняемые российскими участниками проекта

- Приготовление новых пост-металлоценовых катализаторов и новых агентов – переносчиков цепи для их последующего изучения в США и высокопроизводительного тестирования в Германии (первый и второй год).
- Оптимизация синтеза наиболее удачных пост-металлоценовых катализаторов и новых агентов – переносчиков цепи с целью наработки укрупненных образцов полимеров (третий год).
- Приготовление модельных полиолефинов путем контролируемой полимеризации бутадиена с последующим гидрированием. Эта деятельность будет осуществлена совместно с Университетом Цинцинатти (первый, второй и третий год).

Научные работы, выполняемые зарубежными участниками проекта

- Новые катализаторы полученные из Москвы будут протестированы в полимеризации этилена и пропилена в условиях суспензионной полимеризации (Dr. Nagy, Цинцинатти, США), в условиях гомогенной полимеризации (Dr. Piemontesi, G.Natta Research Center, Феррара, Италия), с использованием специальной техники высокопроизводительного тестирования (Dr. Kristen, Франкфурт, Германия) для выявления лучших каталитических систем (первый, второй и третий год);
- Будут приготовлены образцы полимеров, используя комбинации новых катализаторов и агентов-переносчиков цепи (Dr. Nagy, Цинцинатти, США), (Dr. Piemontesi, G.Natta Research Center, Феррара, Италия) (второй и третий год);
- Модельные и новые образцы полимеров будут детально проанализированы с использованием широкого набора аналитической техники (Prof. Beaucage, Dr.Galiatsatos, Цинцинатти, США) (первый, второй и третий год).
- Особое внимание будут уделено использованию современной техники по рассеянию нейтронов для анализа как модельных полиолефинов, так и полимеров, полученных в результате комбинации новых катализаторов и агентов-переносчиков цепи (Prof. Beaucage, Dr.Galiatsatos, Цинцинатти, США) (первый, второй и третий год).

Обоснование целесообразности выполнения работы именно с этим зарубежным партнером

- Несколько лет назад установлены плодотворные рабочие контакты между научной группой из Москвы (проф. И.Э.Нифантьев) и научным подразделением LyondellBasell (Dr.Nagy и Dr.Piemontesi); несколько лет существует сотрудничество между Университетом Цинцинатти (Prof. Beaucage) и американским научным подразделением LyondellBasell (Dr.Galiatsatos, Dr.Nagy);
- В ходе осуществления синтетической части проекта будет синтезировано большое количество весьма перспективных катализаторов. К сожалению, в России в настоящее время практически невозможно осуществить их всестороннее тестирование (нет техники, специалистов). Участие коллег из США, а также специалистов из компании LyondellBasell – технологического лидера в данной области, позволит провести по-настоящему исчерпывающее изучение катализаторов, синтезируемых в Москве;
- В ходе осуществления полимерной части проекта будет синтезировано большое количество уникальных полимеров, обладающих особой архитектурой. К сожалению, в России в настоящее время практически невозможно осуществить их

всестороннее исследование (нет техники, специалистов). Участие коллег из США – признанных экспертов по исследованию свойств полиолефинов методами рассеяния нейтронов и другими современными методами, позволит выявить уникальные особенности полученных полиолефинов с особой архитектурой;

- В Университете Цинцинатти, а также в лабораториях LyondellBasell имеется исчерпывающий набор техники для исследования полиолефинов, включая доступ к SANS и новому HFIR. В ходе осуществления настоящего проекта российские участники получат некоторый доступ к ней, что приведет не только к достижению конкретных научных результатов, но также и к знакомству российской стороны с современными методами анализа полимеров;
- Prof. Beaucage и Dr. Galiatsatos обладают уникальными знаниями и методами анализа молекулярных и супрамолекулярных структур, на синтез и изучение которых нацелен настоящий проект [20,21]

35.6. Ожидаемые по окончании проекта научные результаты

По завершении проекта предполагается достигнуть следующих результатов:

1) Будет разработан новый класс современных моноцентровых катализаторов полимеризации, характеризующийся высокой активностью и низким вкладом процессов переноса цепи. Ожидается, что будет осуществлен режим «живой» полимеризации в используемом в промышленности интервале температур. При этом предполагается разработка новых и оригинальных методик дизайна каталитических систем, основанных на компьютерном моделировании процессов.
2) Будут разработаны новые, эффективных и доступные агенты переноса цепи, совместимые с широким рядом функциональных групп. Данная область требует разработки принципиально новых экономически оправданных синтетических подходов к получению такого рода агентов.
3) Будут созданы новые методики анализа и описания структуры полимеров для надежного подтверждения возможности их использования при создании новых материалов, а также установления взаимосвязи между супрамолекулярной/молекулярной топологией целевых полимеров и структурой катализаторов, с использованием которых они получаются.

35.7. Современное состояние исследований по заявленной научной проблеме, сравнение ожидаемых результатов с мировым уровнем

Последние достижения в области координационной полимеризации включают различные комбинации моноцентровых катализаторов, «живые» каталитические системы для полимеризации олефинов при высоких температурах и методики контролируемого переноса цепи, потенциально позволяющие производителям полиолефинов расширять спектр доступных архитектур полимеров [8,9]. В настоящее время в химии катализаторов наблюдается дрейф от металлоценовых к пост-металлоценовым системам, причем структуры многих новых катализаторов включают хелатные лиганды. Пост-металлоценовые моноцентровые катализаторы, для которых удается варьировать эффективность внедрения со-мономера и скорости процессов переноса/обрыва цепи, *теоретически* позволяют реализовывать новые стратегии синтеза полимеров. Разнообразие типов лигандного окружения и обширность экспериментально «еще не освоенных территорий» сулит радужные перспективы в разработке новых типов полиолефинов при одновременном снижении стоимости их производства. Современные расчетные методы и высокопроизводительные экспериментальные техники позволяют проводить эффективные научно-исследовательские работы в этой области. Интегрированная стратегия дизайна – «катализатор-процесс-продукт» требует общих, дешевых синтетических подходов к лигандам-предшественникам, основанных на использовании легко доступных исходных соединений.

В качестве ключевого элемента программы, мы планируем расширить перечень агентов, используемых сейчас в методиках обратимого переноса цепи, за пределы диалкилцинка. В дополнение к поиску более эффективных систем, мы предполагаем исследовать различные пути использования агентов переноса цепи в качестве «проводника» для введения полярных функциональных групп в полиолефин.

В случае удачи, используя существующую технологию, мы создадим новые полимеры с контролируемой микроструктурой.

35.8. Имеющийся научный задел по предлагаемому проекту: полученные ранее результаты, разработанные методы

- у российских участников проекта

Деятельность исследовательских групп под руководством проф. И.Э.Нифантьева на Химическом факультете МГУ им. М.В.Ломоносова сконцентрирована на разработке катализаторов полимеризации олефинов. В течение последнего десятилетия были разработаны удачные синтетические подходы к разнообразным металлоорганическим каталитическим компонентам, в результате чего было синтезировано более 1000 индивидуальных соединений, протестированных в различных полимеризационных процессах, для ряда которых была показана возможность промышленного внедрения [22-25].

Сотрудничество проф. И.Э.Нифантьева со своим американским коллегой и коллективом R&D подразделения LyondellBasel по новым пост-металлоценовым катализаторам уже привело к первым результатам: было показано, что хинолиновые комплексы перспективны в катализе [12-14], поэтому в качестве следующего шага необходимо синтезировать как минимум несколько десятков разнообразных соединений этого класса и исследовать их каталитическую активность.

Независимо, в группе И.Э.Нифантьева ведутся работы по полимеризации диенов на широком круге катализаторов: от анионной полимеризации до координационной – Nd, Co и Ti- катализируемой. В 2009 году был разработан эффективный метод получения гребнеобразных полибутадиенов. В настоящее время разрабатываются синтетические подходы к «звездочным» полибутадиенам.

- у зарубежных участников проекта

Проф. Beaucage и доктор V.Galiatsatos (LyondellBasell, Цинциннати, США) добились важных результатов, которые будут использованы в ходе реализации настоящего проекта:

- Была разработана количественная описания микроструктуры полимерной цепи с использованием малоуглового рассеяния нейтронов [28];
- Был разработан метод количественного описания локальных структурных свойств с использованием рассеяния некйтронов [20,21,28,31-32];
- Проект планирует использовать гибридную методику хроматографического фракционирования, разработанную Dr. V.Galiatsatos (LyondellBasell, Цинциннати) для выделения узких молекулярно-массовых фракций полимеров, полученных с использованием разнотипных каталитических частиц, для более глубокого понимания связи между каталитической активностью и структурой активной частицы.

Проф. Beaucage и доктор V.Galiatsatos располагают уникальными возможностями для анализа и исследования молекулярных и супрамолекулярных структур полимеров, являющихся целью представленной работы [20,21]. Beaucage разработал количественный подход с использованием рассеяния нейтронов и небольших количеств гидрированных полимеров, который может количественно охарактеризовать детали молекулярной топологии, а также макромолекулярную, супрамолекулярную и наноструктуры полу-кристаллических полимеров как функции структуры катализатора и условий полимеризации. В распоряжении проф. Beaucage имеется лаборатория для препаративного приготовления образцов для исследования методом рассеяния нейтронов, подразделения статического рассеяния света, укомплектованные оптическими микроскопами и высокопроизводительными приборами рентгеновского рассеяния, включающими 2 камеры с вращающимся анодным источником, а также ультра-малую камеру углового рассеяния (Bonse-Hart) разработанную Beaucage и студентами старших курсов (финансирование Procter & Gamble). Beaucage также располагает синтетической лабораторией.

Лаборатория доктора Piemontesi's в исследовательском центре «G. Natta» (Ferrara, Italy) занимается исследованиями в области разработки новых полиолефиновых материалов на основе пропилена и бутена [25]. Доктор Nagy эффективно работает в области дизайна каталитических систем с использованием компьютерного моделирования в исследовательском центре LyondellBasell's (Цинциннати, США) [26]. Доктор Kristen руководит высокопроизводительной экспериментальной лабораторией, занимающейся исследованием полиолефинов, в исследовательском центре LyondellBasell (Франкфурт, Германия) [27].

35.9. Список основных совместных публикаций российских и зарубежных участников проекта, наиболее близко относящихся к предлагаемому проекту

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2. Nifant'ev, Ilya E.; Laishevtsev, Ilya; Ivchenko, Pavel V.; Kashulin, Igor A.; Guidotti, Simona; Piemontesi, Fabrizio; Camurati, Isabella; Resconi, Luigi; Klusener, Peter A. A.; Rijsemus, Jos J. H.; de Kloe, Kees P.; Korndorffer, Frans M C1-symmetric heterocyclic zirconocenes as catalysts for propylene polymerization, 1: Ansa-zirconocenes with linked dithienocyclopentadienyl-substituted cyclopentadienyl ligands Macromolecular Chemistry and Physics (2004), 205(17), 2275-2291
3. Три поданных патентные заявки (US + PCT; приоритет июль 2009) в сотрудничестве с группой LyondellBasell (I.E.Nifant'ev, S.Nagy et al.), описывающие новые постметаллоценовые катализаторы

35.10. Список основных (не более 5) публикаций российского соруководителя проекта за последние 3 года

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3. M.Sacco, Ilya E.Nifant'ev, Pavel V.Ivchenko, Vladimir V.Bagrov, Franchesca Focante, Metallocene compounds, US2009221772, Publication date: 2009-09-03
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35.11. Перечень оборудования и материалов, имеющихся у научных групп, необходимых для выполнения проекта

- у российской научной группы

Российская группа проф. И.Э.Нифантьева обладает полным набором оборудования для проведения синтеза органических и элементоорганических соединений в масштабе от миллиграммов до килограммов. Помимо этого, группа имеет оборудование для проведениция полимеризации диенов.

Российская группа проф. И.Э.Нифантьева имеет доступ к достаточно современной технике (ЯМР, ИК, масс- спектрометры) для исследования строения органических соединений.

- у зарубежной научной группы

- Уникальный набор реакторов для полимеризации (Франкфурт, Феррара и Цинциннати) –мульти-реакторная система для высокопроизводительного скрининга; реакторы малого, среднего и большого объема; реакторы для проведения полимеризации в жидкой, газовой фазе и приготовления образцов для анализа.
- Вся основная аппаратура для анализа и характеристики полимеров в исследовательском центре LyondellBasell в Цинциннати (ГПХ, TREF, ЯМР, реометры, ИК Фурье-спектрометры).

Оборудование по изучению рассеяния в лаборатории проф. Beaucage:

:

- 12 кВт Rigaku вращающийся анодный рентгеновский источник с тремя типами малоугловых рентгеновских камер рассеяния.
- Две статичные световые камеры рассеяния с оптическими компонентами Princeton Instruments (2D CCD детектор, разрешение 0.6 - 100 мкм).
- Сверхмалая угловая световая камера рассеяния; 30 мВт HeNe лазер, дискретный сканирующий гониометр с оптоволоконной связью с PMT и компьютером. Уникальная оптика «USALS measurements», разрешение 1 мкм – 1 см.
- Сменная оптика, световоды, 5 мВт HeNe лазер, привод дискретного сканирования с контроллером.
- Динамический световой прибор рассеяния, ALV-500/E/EP (Malvern Instruments) в США, который может быть использован для DLS в растворе для коллоидных суспензий наночастиц определяя гидродинамический радиус из коэффициента диффузии.

Прочее оборудование:

- Malvern RH2000 ротационный реометр
- Dupont Instruments 912 дифференциальный сканирующий калориметр
- Реометр с опцией плавления полимера: реометрический динамический анализатор RDA II TA Instruments, динамический механический анализатор DMA 983 в 410 Rhodes Lab
- Динамический ИК прибор, объединяющий динамический механический анализатор с измерением двойного лучепреломления в ИК области через серию синхронных усилителей для изучения динамических свойств полимеров.
- 4 пиролитических реактора с 6 контроллерами потока массы, снабженные соединительными трубками, нагревательными лентами, нейтрализаторами, наборами фильтров, вытяжным насосом, расположенный в 551 лаборатории инженерно-исследовательского центра проф. Beaucage
- Hitachi S 4000 стандартный FEG SEM с теоретическим разрешением 15 Å, и возможностью определения EDS и FEI XL 30 ESEM-FEG с теоретическим разрешением 15 Å и рабочим давлением 20 мм. рт. ст.

Прочие ресурсы:

- Beaucage является основным пользователем по долгосрочному договору с ESRF по in situ SAXS исследованию с использованием лучевой установки ID02. Работа ведется в сотрудничестве с T. Narayanan (ESRF) и с S. E. Pratsinis (ETHZ). Соглашение гарантирует доступ к синхротронам в течение нескольких недель в год и обновляется через 3 года, в настоящее время остался 1 год текущего пользовательского соглашения.
- Beaucage также имеет рабочее соглашение с двумя линиями потока Advanced Photon Source (Чикаго), UNICAT и DNDCAT.
- Beaucage располагает возможностью работы в Oak Ridge National Laboratory с использованием оборудования малоуглового нейтронного рассеяния (через Greg Smith).
- SAXS измерения постоянно производятся в CHESS (Cornell University) и в SSRL (Stanford University). Beaucage также является членом группы пользователей LSU SAXS, финансируемой NSF (CAMD).

35.12. Сведения о зарубежном со-руководителе проекта (на английском языке)

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Оплачиваемые иностранные участники проекта будут подбираться профессором Gregory Beaucage специально в случае получения положительного решения о финансировании проекта

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