Proposed Projects for Center for Macromolecular Topology

Project 1. Controlling polymer rheological properties using long-chain branching.
(Larson, Beaucage, Hadjichristidis, Mays, Smith/Mays ORNL in kind, Jones NIST in kind)

Project 2. Adsorption, adhesion, and topology of linear and branched macromolecules on curved and flat surfaces.
(Green, Kuppa, Clarson, Laine, Smith/Mays ORNL in kind, Hadjichristidis)

Project 3. Effect of branching on flow-induced crystallization and crystalline orientation of polyolefins.
(Solomon, Beaucage, Breese (Eclipse Film Technology in kind support), Ilavsky ANL in kind, Mays ORNL in kind, Hadjichristidis)

Project 4. Gel structure, molecular aggregation/agglomeration and gelation in colloidal fluids.
(Solomon, Beaucage, Smith ORNL in kind, Jones NIST in kind)

Project 5. Network/reinforcing filler mechanical response.
(Beaucage, Green, Ilavsky ANL in kind)

I/UCRC Executive Summary - Project Synopsis	**Date**: January 19, 2012

Center/Site: Center for Macromolecular Topology/University of Cincinnati and University of Michigan

Tracking No.: **Project 1**	**Phone :** (513)556-3063	**E-mail :** beaucag@uc.edu

Center/Site Director: Gregory Beaucage and Ron Larson	**Type: (New)**
Project Leader: Ronald Larson and Gregory Beaucage **Team:** Nikos Hadjichristidis, Jimmy Mays, Greg Smith/Mays ORNL in kind, Ron Jones NIST in kind	**Proposed Budget**: $150,000/year, In Kind Support $40,000 ORNL, $40,000 NIST

Project Description:

Controlling polymer rheological properties using long-chain branching.

Beaucage has developed a new method for the quantification of macromolecular topology, the scaling method that can be used to analyze small-angle scattering data. The method yields unique parameterization of the average branch length, number of inner segments (branch on branch or hyperbranch content) and quantitative (with error bars) measures of the number of branches, mole fraction branches as well as a number of other parameters. We propose to combine this new method with methods developed in the Larson group for inferring branching structures from linear rheology data and catalyst reaction pathways to improve determination of branching structures in polymers of industrial importance. This will be combined with predictions of nonlinear rheology to determine how to tailor branching levels to obtain optimal processing behavior.

Experimental plan: Develop a series of industry relevant samples to study such as chromium resins or other resins where conventional techniques have resulted in some ambiguity. Identify model systems for study such as star polymers for the study of steric effects. Correlate parameterization from the scaling method with catalyst structure, reaction conditions, rheological behavior and other physical properties of the resins. Use the model data, industry data, and rheological data and modeling to develop better estimates of chain architecture using the scaling model. Measure nonlinear rheological properties important for processing, including extensional rheometry and LAOS, and correlate this to branching structure using available theories.

Related work elsewhere: The Beaucage work is unique in the scattering community, and his methods apply to polyethylene, proteins, cyclics, graphene, hyperbranched polymers, polypropylene, model polybutadiene. The Larson group developed the first computer algorithm for predicting the linear rheology of general long-chain branched polymers, applicable to commercial polymers. Larson's method was extended by the McLeish group to include hyperbranching and nonlinear effects, and the software from the McLeish group is also available to the Larson group through their collaboration. When these most advanced methods are combined with novel experimental methods for inferring branching levels and types from the Beaucage group, the result should be the most thorough and accurate method for assessing long-chain branching and its relationship to properties ever developed.

How this project is different: This use of small-angle scattering combined with rheological measurements and modeling is unique in determining macromolecular topology.

Milestones/Deliverables for the current proposed year:

1. Quantification of industry resins
2. Development of technique using model systems
3. Development of computer software for calculation of plausible molecular architectural distributions
4. Develop an understanding of catalyst/synthesis/structure relationship
5. Develop an understanding of the structural basis for rheology

How the project may be transformative and/or benefit society: The project targets the development of a new method for the quantification of macromolecular architecture.

Research areas of expertise needed for project success:

Neutron Scattering Expertise and expertise in SANS data modeling; rheological testing and modeling.

Potential Member Company Benefits:

Understanding of the synthesis/structure/property relationships for product lines. New ability to distinguish resins using quantificaiton of the molecular architecture.

Progress to Date: Many initial studies have been performed. Pubications can be found at . http://www.eng.uc.edu/~gbeaucag/BranchingPapers.html .	
Estimated Start Date: October 1, 2012	**Estimated Knowledge Transfer Date**: October 1, 2013

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I/UCRC Executive Summary - Project Synopsis	**Date**: January 8, 2012

Center/Site: University of Cincinnati and University of Michigan

Tracking No.: **Project 2**	**Phone :** (734) 763-2445	**E-mail :** pfgreen@umich.edu, Vikram.kuppa@uc.edu

Center/Site Director: Greg Beaucage and Ron Larson	**Type: New**
Project Leader: Peter F. Green and Vikram K. Kuppa, Steve Clarson, Rick Laine **Team:** Greg Smith/Jimmy Mays ORNL in kind, Nikos Hadjichristidis	**Proposed Budget**: $150K/year, In Kind Support $50,000 ORNL

Project Description: **Adsorption, adhesion, and topology of linear and branched macromolecules on curved and flat surfaces.**

The interactions between macromolecules and surfaces play a central role in the applications of polymers, from thin films to composites. Polymer films are important for diverse applications that include lubricating layers, coatings, adhesives, functional materials for organic electronic devices, sensors, and in nanoparticle dispersion and reinforcement. The performance of each technology is dependent on the behavior of the interfacial layers, and the long-term functional and structural stability of the polymer, which are in turn determined by the nature of interactions between polymers and (flat or curved) surface. Consequently techniques and strategies need to be developed to understand the implications of this behavior, specifically with regard to the statistics of polymers adsorbed onto different surfaces in the context of varying interaction strength. Understanding the extent to which the adsorbed structure can be controlled by tuning a combination of chain architecture (chain lengths & distributions, co-monomer content, extent of branching), surface topology (radius of curvature), and interactions is key to enabling the formulation of systems with desired behavior and properties.

We propose to study the adsorption and interactions between linear and branched chains in a melt with flat planar surfaces and with curved surfaces. In particular, model systems that include silica nanoparticles and surfaces of various curvatures will be evaluated to provide heuristics for more complex systems and chain architectures.

Silicon containing polymers are in the core of a large number of current and potential industrial applications where the interfacial characteristics of the polymers control their integration into devices. Using new chemical approaches developed by Clarson and Laine to control the topology will be coupled with neutron reflectometry/molecular dynamic simulation methodology

Experimental plan: Polymer-surface interactions will be investigated using atomic force microscopy, dielectric spectroscopy and spectroscopic ellipsometry (P. F. Green), in combination with topology-altering Monte Carlo molecular simulations using sophisticated chain scission moves (V. K. Kuppa). The combined approach of experimental and simulation techniques will enable a fundamental understanding of polymer adsorption and topology across a range of length- and time-scales.

Develop a series of Si based co-polymers with industrial relevance and controlled tunable topology including size, branching and rigidity of the segments. Study their interfacial structure and dynamics by neutron reflectometry, a unique methodology that allows none-destructive investigation of internal and interfacial structure of the polymers. Correlate the interfacial structure and dynamics with bulk motion of the polymers. Correlate the neutron results with molecular dynamic simulations.

Related work elsewhere: NSF currently funds our research on the structure and dynamics of star shaped molecules. DOE funds research on the structure and dynamics of polymer nanocomposites. This research evolves abound the dynamics of chains, coarsening phenomena, surface plasmon effects, and morphology.

Neutron techniques are among the most effective non-destructive methodologies to analyze structure and dynamics of polymers and probe internal interfaces. Clarson has been a leader in developing methodologies for synthesis of silicon containing polymers of industrial significance with well controlled topology. Together the team is uniquely situated to impact the understanding of the topology effects on polymers with high industrial impact.

How this project is different: The adsorption, adhesion and friction studies are proposed here to be conducted on polyolefin based systems. Research currently supported by DOE-BES and by NSF is complimentary. We would take advantage of science learned from projects funded by NSF and DOE.

This project is unique in using neutron reflectometry coupled with molecular dynamic simulation to elucidate the correlation of topology of silicon containing polymers to their interfacial behavior.

Milestones for the current proposed year: Synthesis and fabrication of samples. Preliminary data on the systems proposed above will be provided. Please note that we are open to studying other systems that may be more relevant to products.

1. Synthesis a relevant series of Si based polymers with well defined topology
2. Extract interfacial effects as a function of the topological evolution of the polymers.
3. Develop an understanding synthesis/surface structure/surface dynamics/topology relationship

Deliverables for the current proposed year: New information and insight into adsorption, adhesion, layer structure and dynamics, and topology.

How the project may be transformative and/or benefit society: Polymer films and polymer nanocomposites are used in technologies that rely on the long-term structural stability and properties of the films. The proposed study will discover and provide new insights into the interactions between polymers and surfaces, which impact the behavior of a variety of scientifically and industrially relevant systems.

Research areas of expertise needed for project success: Polymer Physics; knowledge of the structure and properties of polymer films; use of appropriate experimental techniques to probe the properties of polymer thin films; knowledge of statistical mechanics and/or molecular simulations Synthesis, Neutron Scattering Expertise and Molecular Dynamic Simulations.

Potential Member Company Benefits: New information and insight into adhesion and adsorption, which are important in a range of technologies.
Understanding of the synthesis/structure/property relationships for new product lines. New ability to distinguish interfacial behavior impacting the integration of polymeric materials into devices.

Progress to Date: We have the expertise to perform these experiments. Experiments have not yet begun. Simulations have been performed on linear homopolymers interacting with flat surfaces. Role of comonomer content and surface curvature is expected to be undertaken.

Estimated Start Date: October 1, 2012	**Estimated Knowledge Transfer Date**: October 1, 2013

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I/UCRC Executive Summary - Project Synopsis	**Date**: January 19, 2012

Center/Site: University of Michigan

Tracking No.: **Project 3**	**Phone :** (734)936 -0772	**E-mail :** rlarson@umich.edu

Center/Site Director: Ronald Larson and Greg Beaucage	**Type: New**
Project Leader: Michael Solomon, Greg Beaucage, Ryan Breese (Eclipse Film Technologies) **Team:** Ryan Breese (Eclipse Film Technology in kind support), Jan Ilavsky ANL in kind, Jimmy Mays ORNL in kind, Nikos Hadjichristidis	**Proposed Budget**: $150,000/year, , In Kind Support $75,000 Eclipse Film Technology, $25,000 Argonne, $25,000 ORNL

Project Description: **Effect of branching on flow-induced crystallization and crystalline orientation of polyolefins.**

Long and short chain branching in polyethylene and other polyolefins have dramatic effect on the degree of crystallinity, the structure of polymer crystallites formed in processing flows and on the level of orientation of the semi-crystalline structures that form. This project seeks to leverage the understanding developed in Project 1 concerning the structural and rheological details of model and commercial polyolefins towards a more full understanding of the implication of these structural and rheological properties on crystallization in processing flows. The project will take advantage of expertise at the University of Michigan and Cincinnati as well as expertise at Argonne National Laboratory at the Advanced Photon Source (APS) where in situ x-ray scattering studies of crystallization under shear and under machine direction orientation of polymers films will be studied in collaboration with Eclipse Film Technologies.

Experimental plan: Use polarized light scattering, polarized light microscopy, small and wide angle x-ray scattering, polymer modeling and mechanical rheology to quantify the effect of branching, particularly long chain branching, on the crystallization kinetics and morphology of polymer melts crystallized under various flow and thermal profiles. The structural measurements will directly characterize the evolution in crystallite size, shape, number density, and orientation so that the effect of long-chain and short-chain branching on these structural properties can be discovered. These structural properties are directly related to final use properties of polymers, including their impact toughness. Machine direction orientation in polyolefin films will also be studied using the same techniques and in situ SAXS at the APS

Related work elsewhere: The study of flow-induced crystallization in model linear polymers, as well as in commercial polymers, such as polypropylene, by techniques such as scattering and rheology is well developed. There has been initial work on the effect of molecular architecture and branching structure (e.g. P.K. Agarwal et al, "Shear-induced crystallization in novel long chain branched polypropylenes by in situ rheo-SAXS and -WAXD," *Macromolecules*, **36**, 5226 (2003); E.L. Heeley et al., "Shear-induced crystallization in blends of model linear and long-chain branched hydrogenated polybutadienes," *Macromolecules*, **39**, 5058 (2006).) Beaucage has published in this area in collaborative work with LyondellBasell over a number of years, J. of Polym. Sci. B **39**, 2923-36 (2001); **45**, 1834-44 (2007); **46**, 607-18 (2008); Polymer **42**, 3103-13 (2001); **44**, 1103-15 (2003); Curr. Opin. In Sol. St. Mat. Sci. **8** 436-48 (2004). These papers detail the use of SAXS and WAXS to understand the relationship between the properties of polyolefin films and the nano- and crystallographic structure.

How this project is different: This project is different because of: 1) the comprehensive suite of experimental and modeling tools that will be applied to the problem; 2) the plan to study materials in which features of long-chain branching are homologously varied leveraging materials synthesized for Project 1; 3) the plan to study blends of well-characterized branched and linear polyolefins; 4) collaboration between three teams with expertise in characterization and processing at Michigan, Cincinnati and Eclipse Film Technologies.

Milestones for the current proposed year: 1) Within six months, have integrated scattering, microscopy and rheologoical measurements of a model branched polyolefin so as to quantify the effect of shear deformation on the crystallite structure (crystallite size, shape and number density). 2) Within one year, have studied a homologous series of long-chain branched polyolefins by scattering, microscopy and rheology, so as to quantify the effect of long-chain branch density on the aforementioned polymer crystallite properties.

Deliverables for the current proposed year: 1) Integrated experimental methods for characterization of flow and thermal effects on the crystallization of polyolefins by means of light scattering and rheology; 2) Correlation of the effect of long-chain branching density on crystallite size, shape, number density and orientation as a function of shear deformation for polyolefins.
How the project may be transformative and/or benefit society: Improved control of mechanical, transport and impact properties offered by long-chain branching effect on crystallite morphology, including size, number density and orientation, can yield polymer properties with improved impact and failure properties.
Research areas of expertise needed for project success: Polarized light scattering; X-ray scattering; polarized light microscopy; mechanical rheometry, synchrotron SAXS/WAXS, polymer processing.
Potential Member Company Benefits: 1) Improved ability to link long and short chain branching structure to crystallization kinetics and crystallization morphology of polyolefins; 2) Potential to manipulate crystallite morphology (e.g. size and density) by means of polyolefin branching structure; 3) structural control over crystalline orientation in processed polyolefins.
Progress to Date: Methods and materials are in place to execute this project

Estimated Start Date: October 1, 2012	**Estimated Knowledge Transfer Date**: October 1, 2013

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I/UCRC Executive Summary - Project Synopsis	**Date**: January 19, 2012

Center/Site: University of Michigan/University of Cincinnati

Tracking No.: **Project 4**	**Phone :** (734)936 -0772	**E-mail :** rlarson@umich.edu

Center/Site Director: Ronald Larson and Greg Beaucage	**Type: New**
Project Leader: Michael Solomon, Greg Beaucage, Rick Laine, Steve Clarson **Team:** Greg Smith ORNL in kind, Ron Jones NIST in kind	**Proposed Budget**: $150,000/year, , In Kind Support $40,000 ORNL, $40,000 NIST

Project Description: **Gel structure, molecular aggregation/agglomeration and gelation in colloidal fluids.**

Molecular aggregation, gelation and the structure of gels are of great importance to colloidal rheology for consumer products, network formation in elastomers and for hyperbranched polymers. Our current understanding of network structure fails to describe known structural quantification from scattering measurements. This project seeks to coordinate efforts to understand network structure and rheological behavior in complex colloidal fluids. The project will identify relationship between rheological enhancement, polymer microstructure, and polymer chain chemistry with gel structure and quantification of the network structure. This project will take advantage of synthetic expertise at Michigan and Cincinnati for the production of model network structures as well as studying in parallel materials of commercial interest such as acrylic gels, elastomeric systems and other networks and highly crosslinked systems of interest to the IAB. The approach will couple characterization and modeling with synthetic capabilities to develop an understanding of structure property relationships in network systems.

Experimental plan:.

1) Develop scattering and rheological methods to characterize aggregation in water borne polymers, particularly those with hydrophobic structure, or produced from bacterial sources
2) Apply experimental methods developed to industry selected polymer systems.
3) Develop a series of industry relevant samples to study synthetic control over gel topology and its effect on gel properties. These samples will be swollen with deuterated solvent and measured using SANS at Oak Ridge National Laboratory and at NIST. Fitting parameters such as the molecular weight between crosslinks and the network functionality obtained using the gel-tensile blob model will be compared with synthetic conditions and properties.

Related work elsewhere: Conventional measures of network structure include measurement of the swelling ratio using the Flory-Rehner theory. This approach has not produced a viable understanding of the structure/property relationships since it is based on a structure (Gaussian chain) that is not observed experimentally. Similarly, the c* theorem can be used to predict some properties but has no structural basis.

Characterization of chemical and chain properties of aggregating polymers is widespread. However, most studies of aggregation due to attractive interactions occurs in the area of colloidal particles not for networking polymers.

How this project is different:. This project combines polymer chemical and chain characterization with microstructural measurements of aggregation so as to acquire a complete microscopic picture of the system. This information can then be correlated with rheology.

This project uses a new structural model, the gel tensile bob model, that has been demonstrated to reflect the structure of equilibrium swollen polydimethylsiloxane gels. We seek to apply this new structural model to industry relevant gels and to model networks to determine structure property relationships

1. **Milestones for the current proposed year**:
2. SANS measurements
3. SANS data reduction and fitting
   Comparision with synthetic protocol and physical properties
4. Select water-borne polymer system of industrial interest
   Generate "phase diagram" of chain aggregation properties of the system as a function of polymer chemistry and solvent conditions

Deliverables for the current proposed year:

1. Water-borne polymer aggregation phase diagram.
   Measurements of aggregate size to correlate with future measurements of system rheology
2. Development of an industry driven set of model samples for structure/property studies
3. SANS measurements on gels swollen in deuterated solvent
4. Modeling of the SANS data with the Gel-Tensile Blob Model to generate molecular weight between crosslinks, crosslink functionality and thermodynamic characteristics of the gels
   Coupling of SANS results with our understanding of the sample history as well as the gel properties

How the project may be transformative and/or benefit society:. Understanding the structure of swollen networks is of importance to a wide range of materials from shampoo to diapers and including biological materials and many materials of industrial relevance.
Water-borne polymers such as to be studied in this project are an increasingly important material class because products comprised of them have reduced environmental impact due to the change from organic to aqueous solvent system. These polymers also have the potential for procurement from natural sources (e.g. bacterial production), as opposed to production from petroleum-based resources.

Research areas of expertise needed for project success:
Neutron Scattering Expertise, Knowledge of Gel Properties and Synthesis
Size-exclusion chromatography, dynamic light scattering, small-angle light scattering, mechanical rheometry. Expertise in synthesis of siloxane polymers will be needed for model studies.

Potential Member Company Benefits:
Understanding of gel product lines and control over gel properties through synthetic protocol.
Improved ability to design and control polymer functional properties in water borne systems.
Ability to link rheological response to underlying aggregate structure as well as polymer chemistry and solvent conditions

Progress to Date: Initial studies have been performed. Publications on polydimethylsiloxane system. General applicability of the research approach has been demonstrated for the particular cases of high molar mass poly(ethylene oxide) (with applications in turbulent drag reduction) and for bacterially produced polysaccharides (with applications in medical devices)

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I/UCRC Executive Summary - Project Synopsis	**Date**: January 19, 2012

Center/Site: University of Michigan/University of Cincinnati

Tracking No.: **Project 5**	**Phone :** (734)936 -0772	**E-mail :** rlarson@umich.edu

Center/Site Director: Ronald Larson and Greg Beaucage	**Type: New**
Project Leader: Greg Beaucage, Peter Green **Team:** Jan Ilavsky ANL in kind	**Proposed Budget**: $100,000/year, , In Kind Support $40,000 Argonne National Lab

Project Description: **Network/Reinforcing Filler Mechanical Response.**

Reinforcing fillers present a complex ramified morphology that has been characterized using various morphological models, chiefly those based on fractal scaling. Prediction of properties from these models has not been successful because simple mass-fractal scaling cannot predict mechanical response since it cannot quantify topological features such as branching. We have recently developed a method to quantify branching using scattering measurements that can be coupled with theories by Tom Witten to predict the mechanical response of isolated aggregates as well as reinforced elastomers. This project couples quantification of aggregate topology with prediction of mechanical and dynamic mechanical behavior and measurement of dynamic properties using facilities at Argonne National Laboratory (APS), Cincinnati and Michigan.

Experimental plan:.

1) Scattering measurement on model aggregate materials including silica, carbon and other inorganic aggregates.
2) Prediction of mechanical response using Witten Theory.
3) Fabrication of elastomer composites using facilities at Cincinnati and at corporate partners.
4) Measurement of dynamic mechanical response at Michigan.
5) Measurement on separate aggregates using AFM at Michigan.
6) Coupling of Cincinnati and Michigan work.

Related work elsewhere:

Extensive work has been attempted to correlate mass fractal dimension with mechanical attributes with little or no success.

How this project is different:.

This project uses new tools developed by Beaucage for the quantification of aggregate structure so that features such as the dimension and length of short circuit paths through the aggregate can be quantified, the number of branches, the number of hyperbranched segments, branch length etc. The parameters are needed to predict the mechanical and dynamic mechanical response of aggregates.

Milestones for the current proposed year:

1) Scattering results from filler nano-aggregates.
2) Prediction of properties.
3) Preliminary production of composites from these materials
4) Initial AFM stuides at Michigan and initial DMA measurements.
5) Demonstration of feasibility of project in first year.

Deliverables for the current proposed year:

Demonstration of feasibility of the scaling approach to predict mechanical and dynamic mechanical properties of reinforces elastomers and isolated aggregates.SAXS

How the project may be transformative and/or benefit society:.

Understanding the structure/property relationships of aggregate materials based on a topological description of the structure could pave the way for the design of improved elastomers.

Research areas of expertise needed for project success:

Scattering, scaling theory, DMA, AFM.

Potential Member Company Benefits: Understanding of structure/property relationships in reinforced elastomers.
Progress to Date: Scaling theory has been applied to in situ measurements of flame synthesis of nano aggregates. We have also studied filled elastomers using a conventional fractal approach. Work in the group of Peter Green has centered on dynamic and static studies of nanoscale aggregates.

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