CLiPS Annual Report - 2012
Context Statement

CLiPS Vision and Goals

The **Vision** of the Center for Layered Polymeric Systems (CLiPS) is to create an integrated program of research and education through the vehicle of a unique microlayering and nanolayering process technology at Case Western Reserve University (CWRU). CLiPS will be a powerful national model for distinguished research and for successful recruitment of American students from diverse backgrounds into the science and engineering workforce. CLIPS partner institutions include the University of Texas at Austin, Fisk University, the University of Southern Mississippi, Northwestern University, the Naval Research Laboratory, Kent State University and the Cleveland Metropolitan School District. The Center Director is Professor Eric Baer. He is aided in the management of the Center by Associate Directors for Research, Education & Diversity, and External Affairs. The strategic plan for achieving the CLiPS vision is focused with the assistance of a diverse External Advisory Board.

CLiPS Partner Institutions

The Center:

- Integrates activities of research platforms with multi-level educational programs to train a diverse American workforce that can meet the challenges of new nanotechnologies.
- Focuses the impact of the integrated research and education activities on national priorities in defense, environment, energy, and health.
- Disseminates the knowledge developed through the integrated Center research and educational activities to the larger audience beyond the partner institutions.
- Serves as a compelling model for expanding relationships between minority-serving colleges and universities with major research universities.

The CLiPS approach strategically integrates polymer science and engineering with research in nanotechnology, optics, laser physics, membranes, energy, device development and other scientific disciplines in a "**polymers-plus**" concept. The multidisciplinary nature of the research program flows naturally into graduate and undergraduate education. Integrated educational programs mirror the polymers-plus idea to introduce modular coursework in emerging cross-disciplinary areas. Students and faculty trained in this area are uniquely positioned to make major contributions to the fields of polymer science and technology, physics, chemical and polymer engineering, and nanotechnology. For example, the research and education partnership between CLiPS and Fisk University is broadening participation of African-American students in the science and technology programs at both universities. To attract undergraduate students to CLiPS REU and graduate programs, the Center is in the process of adding three new HBCUs to the Affiliates Program in addition to our regular recruiting efforts. The REU Program and Affiliate schools have been an important source of graduate students for CLiPS partner institutions. In addition, the Polymer Envoys Program engages high school students from the Cleveland Metropolitan

School District, the East Cleveland Schools, and the Cleveland Heights-University Heights School District, in addition to local school districts at the other major CLiPS partner institutions (UT, Fisk, USM) in the exploration of polymer science and engineering as academic pursuits and eventual careers; this program is serving as a model for the partners to form linkages with local public high schools. CLiPS engaged large numbers of pre-high school students in STEM activities as part of our recruiting effort for the Polymer Envoys Program and to help fulfill CLiPS's educational mission.

Recognizing that personal contacts are an important influence in the career choice of college graduates, CLiPS has established affiliations with non-PhD-granting schools that offer strong undergraduate science and engineering programs to stimulate enrollment of American students in CLiPS graduate programs. In addition to the three current CLiPS Affiliates-Ohio Northern University, Rose-Hulman Institute of Technology, and Youngstown State University-we have added three historically Black-serving institutions (HBCUs.) These new Affiliates are Bowie State University in Bowie, Maryland, Central State University located in Wilberforce, Ohio, and Kentucky State University in Frankfort, Kentucky.

Fundamentally new materials are obtained by forced-assembly of polymers into layers no thicker than the radius of gyration of an individual polymer molecule. CLiPS research activities are organized into four platforms to exploit the microlayer and nanolayer structures: (1) <u>Rheology and New Processing</u> focuses on integrating rheology into the multilayering process, and will explore combinations of rheologically dissimilar materials to create new polymer-based structures; (2) advanced <u>Membranes and Transport Phenomena</u> that exploit the layered hierarchy to achieve unique transport properties; (3) novel <u>Optic and Electronic Systems</u> based on the advanced layered materials, and (4) new <u>Science and Technology Initiatives</u> that probe a fundamental understanding and explore new opportunities for the layered structures.

The Center endeavors to become a unique global resource for the dissemination of knowledge in the area of layered polymeric systems and a national force for engaging audiences at all levels in polymer science and engineering. The Center fosters linkages between academia and industry in order to accelerate the development of new product initiatives.

Highlights of 2011-2012

- The management and operational structure was solidified under the reorganization set forth last year:
    - Two new faculty members were hired, Rigoberto Advincula, as a full professor, and Jon Pokorski, assistant professor.
    - The office of Pamela Glover, the Executive Director for Education and Planning, was augmented by the hiring of a Proposal Developer to assist in developing legacy projects for the Center.
    - Three Associate Directors developed their roles, Lei Zhu for Research, David Schiraldi for Education and Diversity, and Kenneth Singer for External Affairs
    - The two new platform leaders made progress in their research thrust areas, João Maia for Platform I and LaShanda Korley for Platform IV.
- Platform I expanded its flow modeling and rheology studies into a new activity titled, "A Study of Flow Instabilities in Multiplier Dies Including Direct Visualization, Flow Simulation, and a New Interfacial Surface Generator." CAPP, the Center for Advanced Polymer Processing was inaugurated. New studies on microstructures were launched, as well as a new equipment-oriented project that focuses on development of on-line sensors to better understand polymer flow throughout the extrusion system.
- Platform II continued fundamental understanding of transport phenomena in micro- and nano-layered systems by performing systematic experimental and modeling studies to identify the dominant controlling structural variables. Focus areas include solvent-free processing of membranes for gas separation and water purification, high performance barrier materials incorporating liquid crystalline polymers, multi-layered oxygen scavenging membranes, and layered systems with fouling resistance characteristics.

- Platform III explores the science and application of micro- and nano-layered polymeric materials for photonics, optoelectronics, and energy technology. The platform added new investigators in the area of synthesis and optoelectronics. Bob Twieg (Kent State University) will be starting with synthesis of active molecules for the Laser and Optical Data storage project. Lei Zhu (CWRU) has joined the Active Materials project. Chris Ellison (UT) is contributing polymer synthesis to the Laser project. The platform continues to develop optical data storage, all polymer lasers, active materials, and photovoltaics. Notably, an initial patent office action accepted the Bragg reflector claims; the distributed feedback laser claims are being incorporated in a second patent.
- Platform IV continued to focus on the nanoconfinement effect in micro- and nano-layered materials. The multilayered dielectric films have demonstrated high energy density, low dielectric and hysteresis losses, and can operate at high temperatures (~125 °C). These properties have far exceeded those for the current state-of-the-art biaxially oriented polypropylene (BOPP) films. Improvements in mechanical toughness have been demonstrated through a layer-thickness dependent shift in nanodeformation mechanics in multilayered films. Crystal growth and orientation within multilayered films has also been controlled via changes in layer thickness.
- Plans are going forward to develop the STEM Academy. A proposal for a planning grant has been submitted to the NSF Transforming STEM Learning program. Ongoing planning is aimed at keeping our partners engaged, developing pilot studies, and in identifying additional collaborators and funding sources for the program.
- CLiPS added three new HBCUs in the Affiliates program to increase efforts to attract students of diverse backgrounds to CLiPS graduate programs.
- Initiated and supported by CLiPS, João Maia has established the Center for Advanced Polymer Processing (CAPP).
- **CLiPS faculty members and students earned the following honors and awards:**

  Faculty Members –

  Benny Freeman (UT) *– ACS Fellow, 2011, Roy W. Tess Award in Coatings, 2012, PMSE*

  Eric Baer (CWRU) *– CWRU Distinguished University Professor, ACS Fellow, 2011*

  David Schiraldi (CWRU) *– Appointed Peter S. Asseff, Ph.D. Chair in Organic Chemistry in the Case School of Engineering*

  Students -

  Daniel Miller, PhD Candidate(UT) - *First Place winner, SPE 2012 PMAD-SPE Challenge: North American College Student Technical Writing Competition*

  Tiffani Burt, PhD Candidate (CWRU) – *Selected for the Thirteenth National School on Neutron and X-ray Scattering, Argonne National Laboratory and Oakridge National Lab*

  Terrence Mathis, Polymer Envoy (CWRU) -

  National Society of Black Engineers Science Fair - 1st Place Best Engineering Application

  Northeastern Ohio Science & Engineering Fair, 1st Place- Performance, 2nd Place -Engineering

  ASM International Material Science and Engineering Fair – 3rd Place

  De'Andre Stafford-May, Polymer Envoy (USM) – *First Place, Region 1 Science and Engineering Fair, First Place in chemistry, as well as the Army, Navy and Air Force Medals of Accomplishment*

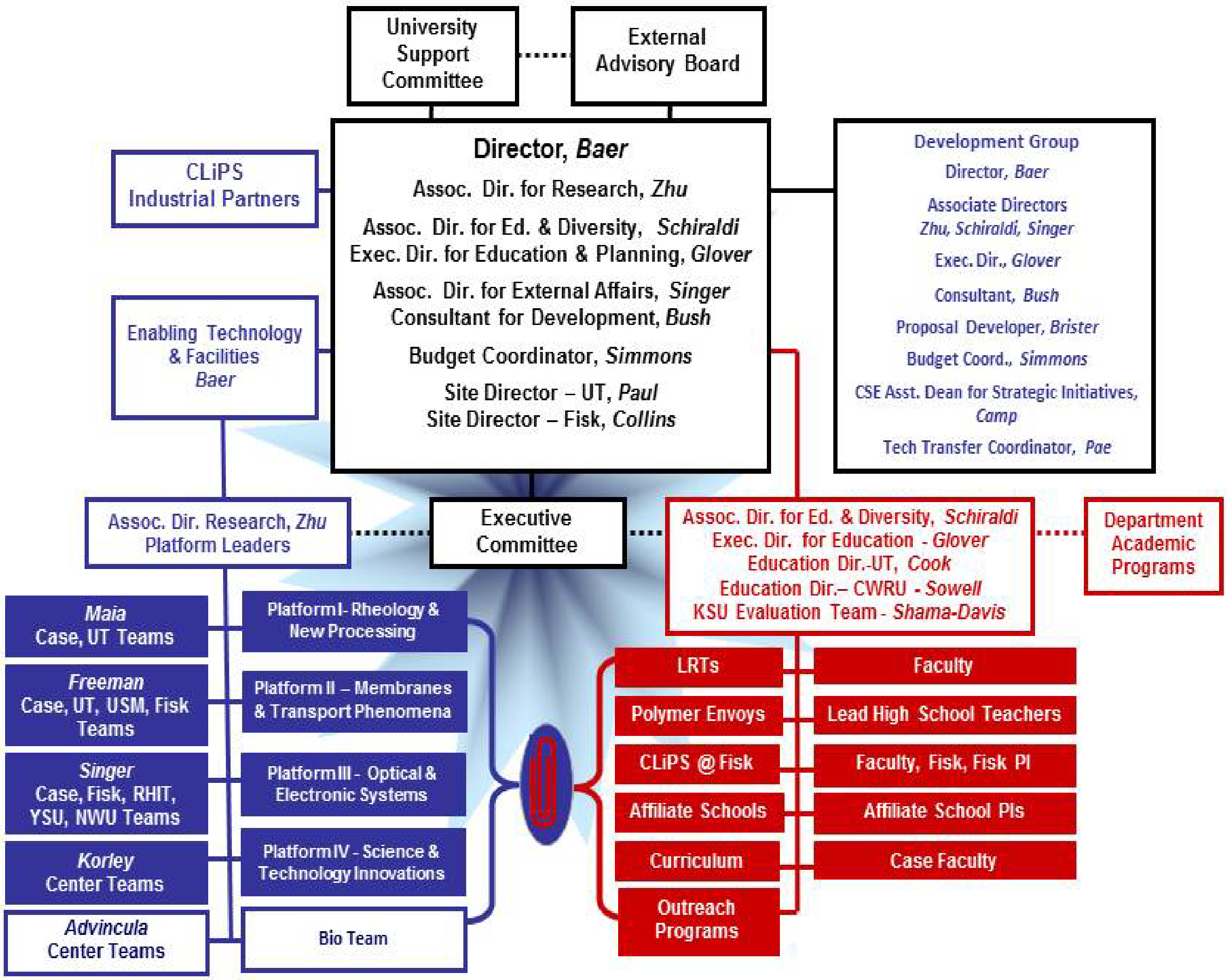
Leadership and Management

The CLiPS organization and operation plan enables the Director and management team to:

- Provide leadership for realization of the Vision through the Strategic Plan
- Ensure integration of multidisciplinary research, education and knowledge transfer activities
- Promote broad participation of the various constituencies that make up CLiPS
- Establish team-based research programs with mechanisms for growth and renewal
- Create a national model for expanding relationships between minority-serving colleges and universities and research universities

- Enable recruitment and education of students with diverse cultural backgrounds into science-oriented careers
- Facilitate education of multi-disciplinary, team-oriented students within traditional university settings
- Maintain effective day-to-day management, fiscal responsibility and reporting functions

The management and operation plan was restructured during the past year as summarized in the Organizational Plan below (see also Appendix B).



The Director, Eric Baer, is a Distinguished University Professor, and Herbert Henry Dow Professor of Science and Engineering. He sets the Vision of CLiPS, leads the strategic planning process with involvement of the membership in an ongoing manner, acts as the intellectual leader in setting research priorities in collaboration with the Platform Leaders, verifies communication across participating groups, ensures integration of diversity throughout CLiPS programs, identifies and mentors new faculty into CLiPS, negotiates fiscal and policy issues with the university on behalf of CLiPS, and makes final decisions on key management positions and resource allocation. With input from the Associate Directors and the Executive Committee, the Director identifies measures for evaluating success in both research and education, and defines indicators of program success. He also leads the industrial outreach and spinoff activities of the Center.

The management team includes the Associate Directors. Lei Zhu, Associate Director for Research, works with the Director to coordinate and develop research activities that extend across the CLiPS research platforms and identifies potential collaborative initiatives that cross platforms and/or institutions. David Schiraldi, Associate Director for Education and Diversity, oversees CLiPS Education and Diversity programs in cooperation with the Director, and provides technical leadership to the Center's educational vision and programming. Kenneth Singer, Associate Director for External Affairs, Associate Director for External Affairs, works with the Director to promote knowledge transfer and commercialization of CLiPS research and technologies, and develops new sources of external funding, enhances Center's outreach and external collaboration.

Pamela Glover, Executive Director for Education and Planning, is a full-time staff member who leads the planning, implementation, assessment and innovation of the integrated research and education programs. She also assists the director in day-to-day management of CLiPS, serves as liaison with NSF, e.g. for Site Visits and Annual Reports, maintains the Center records, assists in public relations and marketing activities, and ensures that the Center operates according to NSF policies for STCs and all federal regulations and statutes. Assisting her in the management of CLiPS's education programs are Tryreno Sowell, Director for Education and Diversity and a full-time staff member at CWRU, and Pamela Cook, Director for Education and Diversity at the University of Texas where she is committed half-time to CLiPS education and outreach programs. This year her office was augmented by the addition of Aaron Brister in the role of Proposal Developer. Mr. Brister provides proposal writing support to both CLiPS research and education activities. Ms. Glover is also assisted by Katherine Binder, Assistant for Operations.

Patricia Simmons, Budget Coordinator for CLiPS, oversees all of the documentation and the fiscal reporting functions of the Center. She is assisted by Jeffrey German-Lortie, Accountant, who is also a full-time staff member.

Dr. Charles Bush serves as a Development Consultant to the Center. He coordinates the intellectual property, industrial outreach and business development activities of the center. He comes from a 32-year career in management of industrial R&D and other technical functions at an executive level. He works with Center faculty to develop industrial collaborations and identify research results that are ready for patent protection.

The committee structure facilitates effective and efficient operation of the research, education and diversity programs while maintaining close communication and interaction between the faculty and staff. The Executive Committee, chaired by the Director, meets monthly with faculty and staff members at the partner institutions via teleconference. The one-hour meetings cover management and organizational aspects of the center and include discussions of the research and education experience of the students and the integration of diversity into the programs.

Technical topics are addressed in regular Platform meetings. The highly interactive research projects require regular meetings for planning and discussion. The platform committees are chaired by the platform leaders and consist of the platform faculty, students and research associates. The flexibility of web-based meetings greatly facilitates inclusion of faculty and students at the partner and affiliate institutions.

The education and diversity programs are coordinated by the Education Program Committee, which meets twice a month to assist the Executive Director for Education & Planning with implementation, translation, and evaluation of the integrated education and outreach programs. The committee membership includes the Director, the Associate Director for Education & Diversity, the Executive Director for Education & Planning, the two Education and Diversity Directors (CWRU & UT), the KSU evaluation team, and the Education Program Coordinators at Fisk University and the University of Southern Mississippi.

The Director is assisted by a diverse External Advisory Board (EAB). Of the 12–member board, two of the members are African-American, two are women, and one has a disability. The EAB meets regularly to review the CLiPS Strategic and Implementation Plan (SIP), to review progress toward research and education goals, to assess the sufficiency of available resources for CLiPS to ensure achievement of the CLiPS integrated research and education mission, and to make a written assessment for the university administration.

Intellectual Merit of the Center

Research Vision and Goals

A broad range of new science and innovation is emerging from CLiPS unique technology. CLiPS is becoming a global resource for microlayered and nanolayered polymeric materials. The CLiPS research activities:

- Define and implement interdisciplinary research programs that exploit the large interfacial area and the unique nanoscale confinement made possible by reducing the dimensions and dimensionality of the layers.
- Use these architectures to create and explore new materials with unique transport behavior, dielectric behavior, and interactions with light.
- Focus the integrated research activities on national priorities of energy, environment, and security.

To achieve these goals, the research programs are organized into four research platforms:

- Rheology and New Processing (at CWRU and UT) enables fabrication of hierarchical microlayered and nanolayered complex polymer-based structures and systems using new feedblocks and multiplier dies, as well as the capability to accurately simulate multi-layered flows inside said equipment.
- Novel Membranes and Transport Phenomena exploit the layered hierarchy to achieve unique transport properties. Researchers from UT, CWRU, USM, and Fisk collaborate in this thrust area under the leadership of UT. We are focused on solvent-free processing of high-flux, high selectivity layered membranes for gas separation and water purification membranes; high performance barrier materials based on forced assembly of nano- and microlayered liquid crystalline polymers and nanocomposite systems; high barrier systems based on multilayered oxygen scavenging membranes; layered membranes with improved fouling resistance; and fundamentals of nanoconfinement on physical aging in layered systems.
- Innovative Optical and Electronic Systems are based on advanced layered materials. Teams from CWRU, Northwestern, Youngstown State, and Rose-Hulman collaborate in the development and testing of devices. The addition of new faculty members from Kent State University and the University of Texas will enhance our exploration of new materials. New work on active materials and polymer synthesis will strengthen the laser and optical data storage projects.
- The layer-multiplying process opens new opportunities for Science and Technology Initiatives. New knowledge and new properties from nanoconfinement effects of micro and nanolayered materials are being studied. Researchers from CWRU, UT, and Fisk are exploring how confined morphologies within multilayered films impact dielectric, mechanical, and crystallization phenomena. Multilayer dielectric films have demonstrated high energy density, high breakdown strength, and low dielectric and hysteresis losses. A new multilayer system also demonstrated high temperature operation up to 125 °C.

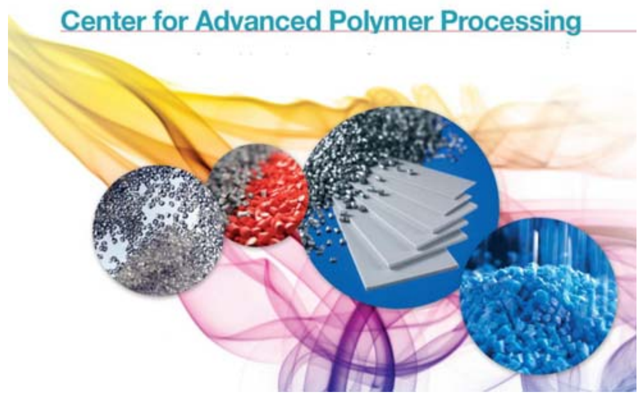
Research Accomplishments and Highlights

In addition to the research platforms described below, the multilayering technology that forms the foundation for CLiPS research is part of the Enabling Technology and Facilities Division that facilitates the needs of all of the platforms under the leadership of the Director.

Platform I: Rheology and New Processing

2011 was a year of strong expansion of Platform I activities, with the "Computational flow modeling" and "Layering of rheologically dissimilar materials", projects being merged into only one entitled "A study of flow instabilities in multiplier dies including direct visualization, flow simulation, and a new interfacial surface generator." Three new projects being launched as well as the inauguration of CAPP-Center for Advanced Polymer Processing and the consolidation of PolymerPlus, a start-up company spun-off the Platform's activity in 2010.

The merging of the first two projects facilitated the management of results, since both projects focused on understanding the kinetics of layer development in the feedblock and multiplying dies.



The "New microstructures" project, led by Eric Baer, effectively developed into three separate projects, one consisting of the original work on fibers and/or fibrillar structures, and the other two dedicated to the possibility of producing layered foams and layered memory-shape materials respectively.

The project on "Extensional rheometry of polymer melts", under the leadership of João Maia, continues to focus on the development of a new dual controlled stress/rate extensional rheometer for polymer melts that will allow CLiPS to perform the full spectrum of rheological characterization of the materials. This capability was achieved in 2011 and the project is now devoted essentially to the characterization and modeling of various polymer systems and no longer on equipment development.

Finally, a new equipment-oriented project was started that focuses on the development of a new series of multipurpose on-line sensors for the monitoring of the evolution along the extruder of the morphological development, as well as the rheological, physical and chemical behavior of multiphase polymer systems. Since one of the main research thrusts of the Platform is to expand the range of materials that can be layered, including polymer nanocomposites and blends, it was felt it was necessary to understand and control the morphology at the exit of the feedblock/multiplying die entrance.

Organizationally, 2011 also saw the creation in November of CAPP-Center for Advanced Polymer Processing. This is a consortium between CWRU, CLiPS and various companies and is a state-of-the-art center for advanced polymer blending and compounding and reactive extrusion able to perform basic non-competitive research and development in the area of materials development and manufacturing by intent in support of the polymer, pharmaceutical and food industries.

Overall, it can be stated that the activities of the renewed Platform I are progressing very well and according to the timeline that was anticipated. We expect to reach steady-state in terms of equipment and publications I 2012.

Platform II – Membranes and Transport Phenomena

Fundamental understanding of transport phenomena in micro- and nano-layered systems will be developed by performing systematic experimental and modeling studies to identify the dominant controlling structural variables. This understanding of fundamental transport phenomena will be used to design and optimize unique layered systems. Layered material systems will be optimized to exhibit trans-port-property profiles that may be otherwise inaccessible. For example, these layered systems may be used for modified atmosphere packaging for products such as meat and produce, and for high barrier applications such as packaging for electronic devices or pharmaceuticals. Further studies involve designing specialized membranes for separation applications such as desalination systems and the development of anti-fouling devices. The anti-fouling technology is being commercialized through the UT start-up company, Advanced Hydro, and research is continuing on additional filtration applications. It is important to note that the emphasis in the development of these new technologies is to be solvent-less and environmentally friendly.

Development of High Barrier Layered Systems using Particulates

The main goal of this proposal is to explore the potential of multilayer technology for the development of nanoparticulate filled structures with enhanced gas barrier properties. In particular the enhancement of oxygen and water barrier will be the target for applications in the area of electronic packaging. Previous research focused on using nanoparticles to enhance barrier properties. The nanoparticles studied included montmorillonite, synthetic fluorinated mica, chrysotile nanotubes, and graphene nanoplatelets. With each system, upon optimization, significant increases in gas barrier properties were observed. In the last year, the focus has turned to using high aspect ratio mica and phosphate glasses (p-glasses) to enhance barrier properties of multilayered structures

Multilayer Fouling Resistant Membranes

Membranes are attractive for use in water purification because of their ability to remove nearly all water contaminants, their small environmental and spatial footprint, and their economic advantages over alternative technologies. However, a significant challenge facing widespread implementation of membranes for liquid purification is fouling. Fouling is the deposition of matter in a membrane's pores or on its surface that leads to changes in membrane transport characteristics. Dopamine is a naturally occurring hormone and neurotransmitter. Lee et al. recently reported that under alkaline conditions, a dopamine solution undergoes polymerization to form a polymer that mimics the properties of mussel adhesive plaque. The polydopamine polymer will non-selectively deposit onto virtually any surface. The deposition will be on the order of 1-100 nanometers in thickness on nonporous substrates depending on contact time. During this past year, fundamental spectroscopic studies have focused on elucidating the fundamental structure of polydopamine, since there is controversy in the literature over its exact structure. Also, we developed a constant flux filtration system and validating it, giving us a new way to study fouling under practically relevant conditions (i.e., constant flux).

Multilayer Desalination Membranes

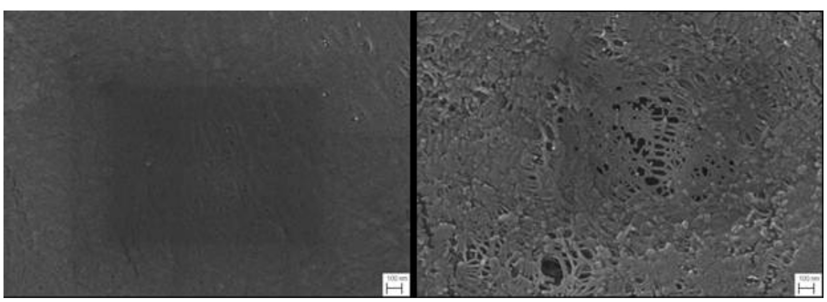
All desalination membranes currently in use are produced via solution processing of monomers that undergo an interfacial reaction at an oil/water interface to produce aromatic polyamide interfacial composite membranes. Large volumes of volatile, flammable hydrocarbon solvents are used in this process. Solution-based preparation is dangerous, and the costs associated with disposal of waste material are high. Thus, there is a great need for better methods for preparing desalination membranes. The goal of this research project is to develop solventless, melt-processible, coextruded membranes for desalination. A multilayer coextrusion process is envisioned to prepare disulfonated poly(arylene ether sulfone) (BPS) thin film composite membranes for desalination. By making membranes via coextrusion, it may be possible to achieve high quality BPS thin film composite membranes at lower cost with more efficient processing. One project, centered at UT, is aimed at developing melt processing protocols for desalination membranes and testing the water and salt transport properties of such materials. Another project, centered at Fisk, is aimed at synthesizing the next generation of materials for this application. At UT, the rheology of blends of BPS materials with plasticizer, based on poly(ethylene glycol) was characterized, and conditions were identified which would enable co-extrusion of plasticized BPS with polypropylene. It was demonstrated that the plasticizer could be extracted following melt processing, and now transport property measurements need to be conducted on these new melt-extruded materials.

Synthesis and Characterization of Novel Chlorine Resistant Polyamide-Polyetheramide Reverse Osmosis Membranes for Desalination of Seawater

This project, headquartered at Fisk University, is complementary to the project above on multilayer desalination membranes, and researchers at Fisk University are exploring new types of polymers for use as desalination membrane materials. Several new types of polymers were synthesized during the past year, and they will be characterized with respect to their water and ion transport properties, at the University of Texas.

Multilayered Materials for Modified Atmosphere Packaging Materials

The preservation of fresh produce as it passes through the supply chain is an important economic and safety issue. Although traditionally achieved through refrigeration, food preservation can also be addressed by controlling the gaseous atmosphere around the produce. This alternative, known as modified atmosphere packaging, or MAP, has recently been shown to be a useful strategy for use with or without refrigeration and has opened up significant opportunities for membrane technology. This project addresses deficiencies of current membranes for this application that ultimately may be solved using layering techniques. The immediate concern is to develop membranes with tunable CO_2/O_2 selectivity. Recent literature reports that poly(ethylene oxide), or PEO, materials have exceptionally high CO_2/O_2 selectivity; however, these materials are not directly suitable for this application, owing largely to their low gas permeability and high water solubility. A line of thermoplastic elastomers produced by Arkema Inc., known as PEBAX block copolymers, are an attractive option for packaging applications. Arkema Inc. generously provided five different grades of PEBAX in pellet form for this investigation. PEBAX 2533 has been coextruded at Case, and initial membrane production and permeation measurements have been made. Films of PEBAX 2533 (80PTMEO-PA12) with thicknesses as little as 7 μm have been achieved, and composite films with selective layers in the tens of microns have been produced. However, thinner films are required to achieve the permeance necessary for packaging; a typical value used in existing packaging is ~ 35 GPU (1 GPU = 1 Barrer/μm) which corresponds to slightly more than 1 μm thickness in some PEBAX grades, and this will represent the processing challenge for the upcoming year on this project. Additionally, we are focusing this project more towards characterization of the porous layers that are required for membrane applications, and this focus is leading us to new applications of microlayering to produce porous membranes for filtration applications and potentially new materials for energy storage applications.



(*Left*) Porous β-iPP film (MFI = 12) as-extruded, stretched at 100°C.
(*Right*) Porous β-iPP film (MFI = 12) annealed at 140°C, stretched at 100°C

Physical Aging of Glassy Polymers in Confined Environments

Polymer glasses and other amorphous materials generally exist in a non-equilibrium state when they are below their glass transition temperature (T_g). In the glassy state, properties such as volume and enthalpy are in excess of their equilibrium values. Physical aging is a term that describes the spontaneous (but typically slow) evolution of these properties towards equilibrium values as the material undergoes structural relaxation. Aging in bulk polymer systems has been studied rather intensively for decades; however, recent observations suggest that the aging behavior of free-standing thin films (<1 μm) and other confined arrangements can differ markedly from that of bulk materials. In free-standing thin films, aging can be orders of magnitude more rapid than it is in the bulk state. This has tremendous practical consequences for polymeric gas separation membranes, many of which achieve separation by permeating gas through a dense glassy layer whose thickness is on the order of 100 nm. The continual decrease in free volume due to aging results in diminishing membrane productivity (i.e., a reduction in gas flux) and modestly increasing selectivity over the lifetime of the membrane module. The practical importance of physical aging effects is not limited to separation membranes; rather, it extends to all applications that utilize glassy polymers in confined environments. Currently, the reasons for the thickness dependence of physical aging are not completely understood. Additionally, the role of interfaces during the aging process has not been well elucidated. It has been theorized that polymer chains near free surfaces (i.e., polymer-air interfaces) have a high mobility compared to material in other areas, allowing them to relax more rapidly. According to this hypothesis, thin polymer films, which have proportionally more near-surface material than thicker films, would undergo accelerated aging in free-standing arrangements. Multilayered films with thin glassy layers can provide a novel means to study the role of interfaces during aging. Extruded multilayered films provide a large number of polymer-polymer interfaces, which will allow us to explore the role of interfacial interactions during aging and will provide new knowledge about the physical aging of polymers in confinement. During the past year, DSC and permeation studies have been used to study physical aging in confined environments, and we are exploring the influence of hard vs. soft nanoconfining layer polymers on physical aging. We have discovered that in the confined nanolayers produced by the multilayer co-extrusion process, aging is very slow, occurring at near-bulk rates. This finding should be beneficial for applications, such as lenses and lasers, which would be sensitive to small changes in refractive index of layers over time.

Oxygen Scavengers for Packaging Applications

Polymers containing unsaturated alkene bonds, such as polybutadiene, offer possibilities as oxygen scavenging materials. In this research, block copolymers, containing polybutadiene, which can be activated for oxygen scavenging, and polystyrene, which assists in blending and melt processing applications, were used as the basis for preparing novel oxygen scavenging systems. These materials were characterized with respect to their morphology and oxygen scavenging characteristics. We are now pursuing melt processing of oxygen scavenging materials and are modeling the performance of such systems.

High Barrier Multilayered Films from Liquid Crystalline Polymers

Liquid crystalline polymers (LCPs) have among the highest barrier properties of all known families of polymers. However, they are typically expensive and can pose melt processing challenges (low melt viscosity with strong temperature dependence of viscosity). In this study, we seek to prepare multilayer films where 1 layer is a high barrier LCP and the other is a confining polymer. We will seek to understand whether the concepts discovered in confined crystallization can be extended to LCPs to reduce the amount of LCP needed to attain high barrier properties and enhance barrier properties via confined "liquid crystallization". Strategies have been identified to markedly increase the viscosity of LCPs, and this is very helpful to make these materials suitable for multilayer coextrusion.

Multilayered Polymer Films for Controlled Release of Small Molecule Therapeutics

This is the newest project in Platform II and is just now getting under way. The sustained release of chemotherapies from polymeric carrier vehicles is a burgeoning area of research in the development of improved cancer treatments. Numerous polymer-based delivery systems have been explored for this purpose including nano- and microparticles as well as layer-by-layer assembled films. In this project, one goal is to fabricate multilayered biodegradable polymer films with varied layer thickness and composition that incorporate one or more small molecule chemotherapeutics. A second goal is to investigate the release rate of small-molecule drugs from varying polymeric film formulations and their subsequent stability and therapeutic activity. Additionally, the project will focus on evaluating the potency of polymer films both in tissue culture and animal tumor models.

Platform III - Optic and Electronic Systems

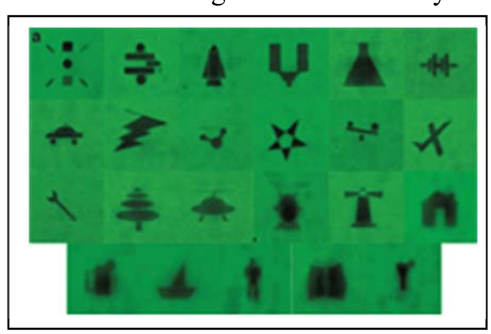
Platform III continues to make excellent progress on its projects: 1) Light Emission and All-Polymer Lasers 2) Optical Data Storage 3) Electro-Optics 4) Active Materials 5) Photovoltaics 6) Coherent Multilayer Effects 7) Antireflection Films and 8) Microlens Fabrication. The GRIN Optics project was spun out of the center funded by other agencies. The Magneto-Optic project was incorporated in a new project aimed at studying coherent optical effects in multilayer films. Major accomplishments this year include successful demonstration of multilayer optical data storage using a Blu-ray laser and enhanced laser efficiency and tunability using a folded distributed feedback structure. Commercialization activities in optical data storage have commenced, including a provisional patent. A patent application was submitted for distributed feedback lasers. A demonstration in the Electro-Optics project is expected in the coming year. Other activities are aimed at enhancing multilayer GRIN optics with antireflection coating and surface patterning, and in the development of improved materials and properties for lasers and optical data storage.

Light Emission and All-Polymer Lasers

The Light Emission and All-Polymer Lasers Project is now being led by James Andrews at Youngstown State University along with Kenneth Singer. The project has completed its demonstration of a tunable elastomeric laser, found to be tunable over a 50nm range by stretching. The distributed Bragg reflector laser is formed by folding an undoped elastomeric multilayer Bragg mirror over its laser-dye doped skin layer. The work was published and highlighted by the editor of Optical Materials Express. Defect lasing in distributed feedback lasers has been studied by simply folding a distributed feedback laser forming a double-thick layer in the center. This defect is shown to lower threshold, increase efficiency, and allow fine control over the output wavelength. Efficiencies of over 30% have been observed. A manuscript has been submitted. These folding concepts suggest a new type of “origami” laser, which will find continued attention. Scientific attention now turns to lifetime issues with the initiation of mechanistic studies, as well as synthesis of new materials. Professor Twieg will contribute members of a class of highly stable fluorophores he has investigated for bioimaging purposes, and Chris Ellison will contribute dye-functionalized polymers also aimed at improving stability.

Optical Data Storage

The Optical Data Storage Project led by Jie Shan and Kenneth Singer has achieved a major goal of demonstrating multilayer data storage. A multilayer film containing a fluorescent dye was the substrate for writing 23 layers of data as shown in the figure. Each of the shapes was written directly on top of each other using a Blu-ray wavelength continuous wave laser. This is the highest number of layers written in layered medium that has been reported. The data was written using a single photon process with the data being a region of quenched fluorescence. It was shown that the data was written at the diffraction limit. These results suggest the possibility of terabyte level data storage in multilayer Blu-ray disk format. As the medium is derived from a continuous multilayer tape, it may be possible to form a petabyte level medium in multilayer tape format. Work continues to find improved writing media less susceptible to erasure during reading.



Electro-Optics

Progress continues in the Electro-optics project, led by Tobin Marks. Amphiphilic dyes synthesized last year have been incorporated into bilayer solvent cast films and polar alignment demonstrated through second harmonic generation measurements. The measured second harmonic susceptibility of the monolayer aligned at the interface between a hydrophobic and hydrophilic polymer indicates a substantial fraction of the dissolved chromophores were well-aligned at the interface. This is a basic level proof-of-principle and suggests that work proceed toward multilayer films. If the layers prove additive, a remarkable new nonlinear optical material will have been demonstrated. We expect to carry out this demonstration in the coming months. Work also proceeds for understanding the alignment and nonlinear optical physics of such a structure as well as in the synthesis of chromophores with enhanced response.

Active Materials

The Active Materials project led by Lei Zhu focused this year on synthesizing polymer brush grafted silver nanoparticles for use in the optical data storage project and on improved chromophores for polymer lasers and optical data storage media. Polystyrene grafted silver nanoparticles combining reversible addition–fragmentation chain transfer (RAFT) polymerization and in-situ reduction were synthesized and characterized. Polystyrene coated silver nanoparticles were also made using seed emulsion polymerization. In the former case, both spherical and rod-like particles were prepared. Finer control over structures is proceeding, and evaluation as optical data storage media will be done in the coming year. The class of DCDHF dyes previously developed for biological imaging is being investigated for use in polymer lasers since they have been shown to have good stability against photochemical damage. These dyes have also been used this year to elucidate the physics of cavity polaritons as part of the photovoltaics project.

Photovoltaics

The Photovoltaics project led by Kenneth Singer has focused on polymer photovoltaics, and specifically on the how optical cavity polaritons can enhance efficiency by increasing efficiency in ultrathin devices. Cavity polariton effects increase absorbance, but also have important spectral implications. We have found that the large absorption in organic polymers and dyes allows for strong coupling in weak cavities. We have exploited this in polymer photovoltaic devices and are preparing a manuscript on this subject as well as on strongly coupled lossy cavities. Synthetic work is focused on high efficiency small molecules organic photovoltaics.

Coherent Multilayer Effects

A manuscript on the effects of slow light on magneto optic effects is currently in press. Work this past year has focused on other coherent multilayer optical effects with CLiPS films such as appliques for enhancing short wavelength sensitivity of optical detectors and for extending the wavelength range of semiconductor lasers. Coherent perfect absorption is also being investigated in relation to folded CLiPS films and laser media. New directions will focus on using optical coherence effects as a characterization tool for film and materials properties in CLiPS films.

Antireflection Films and Microlens Fabrication

Investigation into antireflection films using solution processed silica colloids for use with multilayer GRIN optics is being led by Adam Nolte at Rose-Hulman and preliminary results are promising. Microlens fabrication for GRIN optics microarrays is being explored by Tom Oder at Youngstown State U.

Platform IV - Science & Technology Innovations

Platform IV on science and technology innovations in microlayered and nanolayered materials involves teams from Case, UT, Fisk and NRL who explore new opportunities for the enabling technology under the continued leadership of Professor LaShanda Korley.

One area of focus is the need in power electronic systems and pulsed power applications for dielectric capacitors with high energy density, low losses, and high temperature capabilities. We have achieved a breakthrough by combining a high breakdown strength polymer with a high dielectric constant, PVDF, as multilayer films. The layered films exhibited significantly higher breakdown strength, lower dissipation factor, and low hysteresis. Their superiority was also demonstrated in a couple of prototype capacitors.

Currently, we have achieved understanding of the underlying mechanism of the better performance for these multilayer dielectric films. First, dipole switching is effectively stopped due to nonuniform distribution of electric fields in different layers. The high dielectric constant PVDF layer experiences a lower nominal electric field and the low dielectric constant polymer layer has a high nominal electric field. The low nominal field in PVDF will not be able to switch the dipoles in PVDF crystals. Second, impurity ions in the high dielectric constant PVDF layer play an important role in the hysteresis loss in multilayer films. By confining the ions in nanolayers, the hysteresis loss can be significantly decreased. Third, crystalline lamellar orientation can affect the ionic motion in multilayer films. A flat-on crystal orientation can further reduce the hysteresis loss, as compared to the edge-on crystal orientation. Fourth, interfacial polarization is observed for PVDF multilayer films, especially at high electric fields. These highly charged interfaces are important in enhancing the breakdown strength of multilayer films.

We also investigated high temperature performance of polysulfone (PSF)/PVDF multilayer films. In addition to the effects of different polarizations, electronic conduction due to enhanced charge carrier mobility at elevated temperatures also plays an important role. Therefore, a highly insulating blocking electrode polymer is necessary for high temperature, high energy density, and low loss capacitor applications. Possible candidates are cyclic olefin copolymers and PTFE-based copolymers.

Forced and Self-Assembly

The second focus area aims to combine forced assembly with self-assembly to influence specific function, such as mechanical and barrier properties. Multilayer coextrusion is a unique platform to explore the impact of confinement on the morphology of block copolymers, and the orientation and crystal structure of semicrystalline polymers. Utilizing elastomeric block copolymers confined between alternating layers of glassy polystyrene, we have demonstrated a layer thickness-dependent change in deformation mechanics in multilayer films, shifting from crazing to shear banding with decreasing layer thickness. Upon annealing, unprecedented ordering of the cylindrical block copolymer domains is observed within the thinnest layers. Mechanical anisotropy is also a direct consequence of this ordering and alignment within the multilayered films. Tunable mechanics has been achieved through variations in the confining layer and the block copolymer microstructure. We have also explored the nanoscale deformation mechanisms of confined poly(ethylene oxide) crystals with multilayer films, motivated by the discovery of nearly perfect polymer single crystals obtained by confined crystallization within nanolayers. It was shown the non-uniform micronecking dominates the mechanical response in thin layers, while typical, bulk axial alignment is observed in thicker layers. These promising results motivate further studies of novel block copolymer architectures with embedded functionality as well as polymeric composite materials with tunable responses.

Confined Crystallization

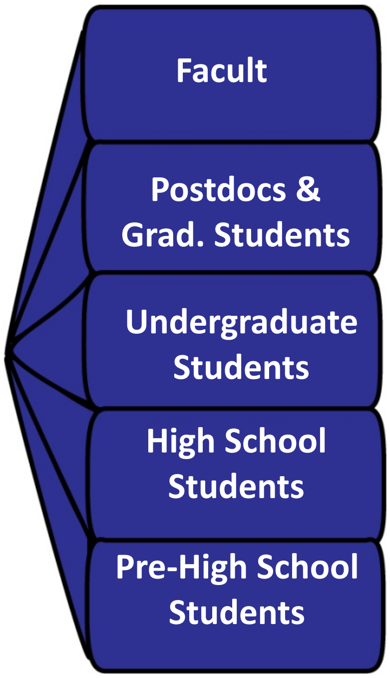
The third focus area addresses the physics of polymers in ultrathin layers. Multilayer coextrusion is an ideal platform to examine long-range, almost defect-free nanoscale confinement, particularly as it relates to crystallization, such as in polyvinylidene fluoride and poly(ethylene oxide).

The research in Platform IV is leading to the discovery and understanding of new structures and new phenomena. These findings can be the basis for more complex hierarchical organizations and new materials systems and explores fundamental questions of confinement-induced phenomena within all Platforms.

Integration of Research and Education

<u>Vision and Goals</u>

CLiPS's vision is to be the global leader for integration of research and education in polymer science and engineering. In order to accomplish this, CLiPS integrates its research with multi-level educational programs to stimulate and prepare American students to pursue professional careers with advanced degrees in polymer science and engineering. The multidisciplinary resources of the Center are employed to develop focused programs that connect and educate a diverse range of American students from middle school through the PhD level.



Just as CLiPS research is based on multilayered structures, CLiPS education programs are called Layered Research Teams (LRT) which are multi-level and interactive in nature.

- Faculty members provide guidance and instruction. They develop project ideas and ensure the efficient operation of the LRT and serve as role models.
- Postdoctoral Associates work under the direction of a specific senior faculty advisor within the LRT. Mentoring is tailored to the career interests of each postdoctoral researcher and includes grantsmanship, interactions with industry and funding agencies, and collaborations with researchers across CLiPS. Postdoctoral associates also fulfill a teaching role interacting with graduate students, undergraduate students and Polymer Envoys on CLiPS research projects.
- Graduate Students conduct research within the LRT. They teach research methodology to more junior students. This combination of teaching and learning activities, with mentoring by the faculty, prepares graduate students to become leaders in the polymer field
- Undergraduates in the LRT are mentored by graduate students on a research projects. They also serve as role models and ambassadors to the Polymer Envoys
- CLiPS program for high school students is the Polymer Envoys program. They are each taught by a graduate student on a longitudinal STEM related project. They share their research and enthusiasm with younger students through activities in the university and local schools.
- Pre-High School Student programs in CLiPS provide opportunities at the university and in the community, for younger students to become excited about science and engineering, and to learn about STEM-related opportunities, such as the Polymer Envoys program.

<u>Mentoring</u>

CLiPS educational programming includes a comprehensive, multi-level mentoring plan which includes Postdoctoral Researchers. This plan is further discussed in the Education section of this report and is found in its entirety in Appendix F.

<u>Postdoctoral Associates</u>

The goals for postdoctoral associates in the Layered Research Team are to:

- Gain experience in identifying best practices and grantsmanship
- Learn the skills to take a leadership role in developing publications, presentations and other knowledge transfer activities
- Enhance professional skills through teaching, interactions with industrial representatives, and with professional organizations

Postdoctoral associates also serve as teachers, mentors and role models for graduate students, undergraduate students and Polymer Envoys in the program.

The success of the postdoctoral associates plan is assessed by monitoring the progress of each associate toward his or her career goals after completing the postdoctoral program. This year, postdoctoral fellow, Mike Ponting, moved into a full time position as the Director of Engineering for PolymerPlus LLC, the CLiPS spin off company located in Cleveland.

<u>Graduate Programs</u>

The goal of CLiPS graduate education is to prepare students as professionals and future leaders in the polymer field. To accomplish this goal, graduate students working in Layered Research Teams enhance their professional development by:

- learning research ethics, safety procedures and skills
- developing professional communication skills
- meeting and collaborating with industrial and academic partners
- participating in regional and national meetings and conferences
- learning to teach by mentoring undergraduate and high school students
- designing and implementing community outreach activities for pre-high school students

This year graduate students were co-authors on 44 of the 50 CLiPS publications in peer-reviewed journals. In addition, this year graduate students and post-docs accounted for 30 of the 82 presentations at local, regional and national meetings.

A key indicator of the Center's success is the production of students who enter STEM careers. During this reporting period, CLiPS graduated four PhDs (for a total of sixteen since the beginning of the Center.) Two of the 2011-12 graduates are in the STEM workforce; one is undecided, and one has accepted a post-doctoral position at CWRU.

Masters candidates at Fisk University fulfill the same teaching-learning role in the LRT as the PhD students. This initiative – CLiPS@Fisk - is addressed in the section on Diversity both here and in the body of the report.

<u>Undergraduate Programs</u>

The CLiPS programs for undergraduate students are the *Affiliates Program* and the summer *REU Program.* These activities expose undergraduate students to polymer research and to opportunities in CLiPS.

CLiPS Affiliates are primarily undergraduate institutions in the states surrounding CWRU which have a strong undergraduate teaching focus and that do not offer PhD programs in CLiPS fields. CLiPS Affiliate institutions are Ohio Northern University, Rose Hulman Institute of Technology, Youngstown State University. In order to help fulfill CLiPS's goal of increasing diversity, we have added three HBCUs to the Affiliates Program. The University of Texas has associations with the UT border schools, UT-Pan American and UT-Brownsville.

The REU program introduces CLiPS technologies, polymer science and STEM research to a diverse group of American students. It is also an important pipeline for American students into CLiPS graduate programs. This year there are twenty students in the program – half of them are women and half are from under-represented groups. Five of them are from the new CLiPS HBCU affiliate schools.

Students work as members of CLiPS Layered Research Teams for ten weeks under the mentorship of a graduate student. In addition to daily research activities, REU students participate in weekly program meetings during which they hone their presentation skills, attend lectures in various areas of polymer science and engineering, and discuss professional ethics. The summer program culminates in the Northeast Ohio Undergraduate Polymer Symposium, an event showcasing the summer research work of undergraduates from CWRU, the University of Akron, Kent State University, and NASA.

High School Program

CLiPS's program for high school students is the Polymer Envoys. This program matches one high school student with one graduate student in a longitudinal relationship that may last two or three years. As a result of this continuity structure, the program provides significant hands-on research experience and mentoring to a small number of high school students. It has a tremendous impact on the individual student participants, and allows CLiPS to more closely track students to determine short- and long-term impacts.

The program was initiated with the beginning of CLiPS in the fall of 2006. At that time six students from the Cleveland Metropolitan School District (CMSD) were recruited to become the first class of Polymer Envoys. The University of Texas followed suit, enrolling four students from the Austin Independent School District in the spring of 2007. This year there are twenty-seven students in the program across the Center. All of the school districts represented in the Envoys program have a high percentage of students who come from under-represented minority groups. The program in Texas also includes students from Texas School for the Deaf in Austin.

To date there have been fifty-eight Polymer Envoys and all but three of them have come from under-represented minority groups. Twenty-seven students are currently enrolled in the program. Thirty-one students have graduated from the Polymer Envoys program; all of them are in college. Twenty-six are studying STEM fields.

In 2008 CLiPS partnered with the Kent State University Research and Evaluation Bureau to study the Polymer Envoys Program. The analysis of the first year's results contained some interesting highlights that will help in planning for the future. A significant finding was the influence of the graduate student mentors on the Envoys. The Envoys reported feeling supported by their graduate student mentor and motivated by the graduate student's academic achievement. They look upon the graduate students as role models both socially and academically. The Envoys reported that they have a long-standing interest in science, but that their high schools do not offer the coursework they need to prepare them for college studies in a STEM field. Tutoring in math and science has been integrated into the Envoys program to help the students in their work in the lab.

Pre-High School Programs

CLiPS is currently engaging youngsters across the Center in activities such as:

- Science Sundays at the Austin Children's Museum reaching greater than 1000 visitors annually
- The Middle School Science Club at Fisk University engaging 30-40 student per year
- Introduce a Girl to Engineering at CWRU, reaching 75 middle school young women
- The Martin Luther King Day activity at the Cleveland Museum of Natural History reaching ~150 children and families

- Summer Science Camp at UT – enrolling 25-30 middle school age students for 2 weeks during the summer
- National Youth Sports Program at CWRU – reaching 80-100 students middle-school age youngsters with interactive science activity sessions held each summer

Integration of Diversity into CLiPS Programs, Projects and Activities

Diversity Vision and Overall Goal

CLiPS aims to become a national resource for broadening participation of women, under-represented minorities, and persons with disabilities in polymer science and engineering and related fields. In order to accomplish this, CLiPS has developed and will continue to develop initiatives that attract, train, and graduate diverse American students into polymer science and engineering, and related fields. The three goals for diversity are:

- To encourage a diverse range of students to pursue STEM careers through pre-college outreach programs and through collaborations between research universities and minority-serving institutions
- To engage Fisk University graduate students in CLiPS research projects through CLiPS @ Fisk activities
- To impact the diversity of faculty, staff, and students at all CLiPS Institutions in a positive way

Engagement of Diverse Students

The Polymer Envoys Program is a key program through which CLiPS engages pre-college students. Working with the Cleveland Metropolitan School District and the Austin Independent School District gives the program ample access to our target populations. Although this program was described elsewhere, it should be noted that all but three of the fifty-eight participants to date have been from under-represented minority groups and half of them have been women.

Guided by experience with the Case-Fisk Alliance, CLiPS is exploring opportunities to engage with other minority-serving institutions. At the University of Texas, CLiPS has developed similar relationships with UT-Pan American and UT-Brownsville, two primarily Hispanic-serving institutions. The University of Texas also has an association with Texas School for the Deaf and hase engaged students there in the Polymer Envoys program and other outreach activities.

CLiPS @ Fisk

Building on the earlier Case-Fisk Alliance, the CLiPS program at Fisk has been broadened and renamed CLiPS @ Fisk. The key components of the program are (1) student involvement focused on MS candidates, and (2) student research involvement with CLiPS projects.

Because Fisk does not have a PhD program in polymer science, faculty members often rely on post-doctoral associates for their research. The change of focus to Master's Degree candidates, identified as CLiPS-Fisk Scholars, has broadened the scope of CLiPS activity at Fisk. In the Layered Research Teams at Fisk this year there are three students who are candidates for a Master's degree, two undergraduate students and three Polymer Envoys. Programs at Fisk include outreach to pre-college and pre-high school students through Saturday Science Academy and middle school Science Club. Finally, coordination of the 3-2 dual degree program between Fisk and CWRU is an important component of the relationship.

Impact on CLiPS Institutions

The Polymer Envoys program is an outstanding example of CLiPS's impact on the institutions involved and is adding to the diversity of the student body at CWRU and UT. In support of Fisk students interested in attending CWRU, two Provost Special Scholarships have been secured to provide financial aid to binary students from Fisk. In addition, CLiPS has actively championed the hiring of women and under-represented minority faculty members (Korley at CWRU; Arnett at Fisk) and will continue to follow that course of action when considering new faculty hires. With CLiPS faculty involvement, the Case School of Engineering has established a program addressing engineering education and outreach, as well as diversity and inclusion components. CLiPS is committed to support such efforts as much as possible.

Partnerships and Knowledge Transfer

The CLiPS goal for Knowledge Transfer is to be a unique global resource for the dissemination of knowledge and technology in the area of layered polymeric systems and the educational programs developed to promote STEM learning and involvement by diverse populations. This requires a complex network of interactions, organized from the standpoints of the: (1) CLiPS participants, (2) Center-related external audiences of government, academic and industrial contacts, (3) and the broader scientific and education communities and the public.

Knowledge Transfer between CLiPS Participants

Meetings

Regularly scheduled administrative and research platform meetings continue to be utilized to meet the Center's goals for knowledge transfer. Web meetings are used to enable effective communication across the different locations of the Center. These regularly scheduled meetings include:

- Weekly or bi-weekly meetings of the platforms
- Monthly meetings of the Executive Committee
- Weekly staff meetings
- Monthly meetings of the Polymer Envoys, liaison teachers and graduate students
- Monthly meetings of the Development Committee

Larger meetings, which also contribute to accomplishing our knowledge transfer goal, include:

- The Annual Meeting of the Center involving CLiPS participants (faculty members, staff members and students) from all sites; held March 15, 2012.
- The External Advisory Board (EAB) meeting on March 15, 2012, coinciding with the CLiPS Annual Meeting.
- In May of 2012, the Workshop on Polymers for Optics and Electronics will be held.

Seminars

Initiated under the ACES program, CLiPS continues to sponsor two seminars on the Case campus each academic year. The speakers for these symposia are either women who are active in academic polymer science and engineering fields or male researchers who have been active mentors to women.

This year's speakers were Benny Freeman from the University of Texas (September 23, 2011), and Charles Sing from MIT (February 24, 2012).

Educational Assessment

The CLiPS educational partnership with Kent State University's Research and Evaluation Bureau, established to study the Polymer Envoys Program, continued during the current year. This work is investigating the characteristics in the targeted high school students' environments that influence their choice of a STEM career and the impact of CLiPS educational programs on these decisions. The initial results have been compiled and analyzed and are being used in our plans to expand the Envoys program within CLiPS and beyond.

Website

A major update to the CLiPS web site is in progress. We have engaged the CWRU IT department to assist with this update.

<u>Governmental, Academic and Industrial Communities</u>

Industrial Showcase/Workshop

Two Industrial Showcase events were held in 2008 and 2010. While attendance at these events was good, the impact on CLiPS programs was less than we had envisioned; therefore, in 2012 we have replaced the Showcase with a workshop concept. The first is being held in May and will focus on Optics and Electronics applications. The second is being considered for the fall of 2012 and the topic is currently being finalized.

Outside Funding - Industry

CLiPS originally projected a goal for outside industrial funding of $2.5 million annually by the end of the Center's five-year period. Research funded by industrial partnerships currently exceeds that amount.

Outside Funding – Government

CLiPS also has attracted significant outside funding from government sources.

<u>Broader Scientific Community and the Public</u>

Professional Meetings and Publications

CLiPS faculty members regularly lead and participate in technical sessions and symposia at scientific society meetings, particularly those of the ACS, SPE and APS. Over the past year CLiPS faculty members and students have had 50 papers published in peer-reviewed journals. CLiPS participants (faculty members, post-doctoral associates, graduate and undergraduate students) accounted for 63 presentations at professional meetings over the past year.

Intellectual Property

During the past year, the *All-Polymer Laser Technology* was granted a patent. A divisional application related to this technology was also filed. Originally covered by provisional patent applications, the technologies for *confined crystallization multilayer films* and *axially oriented confined crystallization multilayer films* were converted to full patent applications. Four new provisional patents applications were filed covering *aspherical GRIN lenses*, *a controlled stress extensional rheometer*, *an advanced multilayer die*, and *multilayer films with high flux and high selectivity*. In addition, the review of two provisional applications resulted in decisions not to proceed with conversion to full patent applications.

Patent activity for the 2011-2012 reporting period is described below:

Patent Issued

1. ***Co-Extruded Multilayer Polymer Films for All-Polymer Lasers, U.S. Patent 7,396,802 -*** *Kenneth Singer, Eric Baer, Anne Hiltner and Christoph Weder*
   This patent covers films which can function as lasers. It is a potential low cost laser technology with a wide variety of applications.
2. A divisional application related to this patent was submitted as a part of its approval.

Full Patent Applications

3. ***Confined Crystallization Multilayer Films*** *- Eric Baer and Anne Hiltner*
   This technology results in high gas diffusion barrier films which potentially are cost effective relative to films currently used commercially. Significant interest exists in this technology for food packaging and other market areas.
4. ***Axially Oriented Confined Crystallization Multilayer Films –*** *Eric Baer, Anne Hiltner, Yijian Lin*
   This patent application is an expansion of the Confined Crystallization application and is a part of the patent estate covering this technology.

Provisional Applications

5. ***Aspherical GRIN Lens -*** *Eric Baer, Ann Hiltner, Michael T. Ponting*
   This application expands the scope of the multilayer technology for GRIN lenses covered in a previous application. It is a key element in the technology being developed for DARPA by the spin-off company, PolymerPlus LLC and has already been licensed to this company.

6. ***Controlled Stress Extensional Rheometer*** *- João Maia, Ricardo Andrade, Patrick Harris*
   For polymer scientists and manufacturers this device significantly expands the capability to characterize polymer melts at a reasonable cost. Its potential users range from research laboratories to manufacturing quality control laboratories.

7. ***Layer Multiplier Die -*** *João Maia, Jorge Silva, Patrick Harris*
   This represents a new design which significantly improves the flow characteristics of polymer melts in these types of systems. It will provide more stable operations and improved quality films and potentially the ability to extrude materials with different rheologies which currently cannot be coextruded.

8. ***High Flux, High Selectivity Multilayer Membranes*** *– Benny Freeman, Eric Baer, Don Paul, Grant Offord, Shannon Armstrong*
   This invention creates films which can be used for selective gas diffusion. These films will have value in food packaging, where selective gas diffusion results in increased shelf life for the packaged food.

Ultimately, the goal of this work is to create commercial technology based on the research and intellectual property developed from the work being carried out in the Center. To this end, two businesses have been created based on work done within the Center. The first, Advanced Hydro in Austin, Texas, is focused on commercializing the patent pending technology to reduce fouling of membranes used for water purification and filtration systems. The second, PolymerPlus LLC in Cleveland, Ohio, is focused on creating GRIN lens technology based on polymer multilayer films and on developing commercial technology and applications for additional patents generated by the Center. PolymerPlus LLC holds a license from CWRU for the Aspherical GRIN lens patent application and for the GRIN lens patent generated by research on multilayer films at CWRU prior to the inception of the Center.

The research and education platforms are actively seeking to leverage their activities through additional support from various funding sources. In 2011-2012, CLiPS received an additional $1 million for continuing research and development of CLiPS patented technology in the areas of energy and defense.

Data Management Plan

CLiPS is a complex Center with many sources of data. To manage the data, CLiPS has elucidated a data management plan that encompasses, among other strategies, the regular channels of peer-reviewed publications and presentations at professional meetings, control of student laboratory notebooks, and the CLiPS website which chronicles publication activity and provides an overview of CLiPS's research and educational programs. The Center's data management plan is discussed further in the Knowledge Transfer section of this report and may be found in Appendix G.

Value-Added of CLiPS

The field of interdisciplinary macromolecular science and engineering has rapidly emerged over the past ten years at the crossroads of polymer science, materials science, engineering disciplines, chemistry, physics and biology. This field of "polymers plus" enjoins inspiration from nature, innovative processing of microlayer and nanolayer polymeric assemblies (forced assembly), and revolutionary new synthetic polymers with greater control of macromolecular and supermolecular architecture (self-assembly). A critical need exists for innovative microprocessing and nanoprocessing technologies to achieve the envisioned materials systems.

The potential application and economic impact of hierarchically organized polymer and hybrid polymer/inorganic layered systems with length scales ranging from a few nanometers to many microns are extremely broad and encompass diverse areas such as healthcare, energy, defense and environment. The expansion of Platform I to include research on understanding and control of polymer rheology will enable combinations of materials previously not possible and lead to structures which can meet performance properties not previously achievable with extrusion technology. This will accommodate the diverse needs of Platforms II, III, and IV and enable them to expand their scope in areas such as membranes and optical/electronic systems and others that are not currently addressed in Platforms II, III and IV.

The broad scope of these research activities requires participation of outstanding researchers and educators in many disciplines, including polymers, optics, electronics, material science, transport, and engineering. CLiPS is uniquely positioned to meet this challenge and has assembled a multidisciplinary, multi-institutional team of investigators. The work of these groups of scientists and engineers is disseminated through the CLiPS Knowledge Transfer program, which provides a vehicle for intellectual exchange with the public and the links to industry will allow for significant technology impact, fostering science and technology in service to society.

Research and education aspects are integrated to create a special environment for discovery, learning and innovation by students at a wide range of levels from elementary grades through graduate level, faculty and associated researchers. Emphasis is placed on teamwork, communication and engagement of students in the research and education activities to make CLiPS a unique place for training a well-qualified academic and industrial workforce. Enhanced diversity and engagement of underrepresented groups is considered a critical component of well-balanced programs and workplaces. CLiPS aim is to exploit the features of modern U.S. society with an emphasis on teamwork, communication, and workforce diversity, in addition to excellence in research and education.