CONTEXT STATEMENT - 2009

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 (Case). CLiPS will be a powerful national model for distinguished research and for successful recruitment of diverse American students into the science and engineering workforce. To create CLiPS, Case has partnered with the University of Texas at Austin (UT), Fisk University (Fisk), the University of Southern Mississippi (USM), and the Naval Research Laboratory (NRL) under the leadership of the Director, Professor Anne Hiltner, and the Co-Director, Professor Eric Baer. The strategic plan for achieving the CLiPS vision is distilled with the assistance of a diverse External Advisory Board.

The envisioned Center will:

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

The CLiPS approach strategically integrates polymer science 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 will be uniquely positioned to make major contributions to the emerging field of nanotechnology.

A research and education partnership between Case and Fisk is broadening participation of African-American students in the science and technology programs at both universities. The Polymer Envoys Program engages students from the Cleveland Metropolitan School District 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.

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. Fundamentally new materials are obtained by forced-assembly of polymers into layers no thicker than the radius of gyration of individual polymer molecule. CLiPS research activities are organized into four platforms to exploit the microlayer and nanolayer structures: (1) unique Enabling Technology that enables fabrication of hierarchical microlayered and nanolayered polymer-based structures and systems; (2)
advanced Membranes and Transport Phenomena that exploit the layered hierarchy to achieve unique transport properties; (3) novel Optic and Electronic Systems based on the advanced layered materials, and (4) new Science and Technology Initiatives 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 2008-2009**

- Discovery of nearly perfect polymer single crystals by confined crystallization of nanolayer assemblies was published in Science.
- An all-plastic distributed feedback laser with low threshold and high efficiency was fabricated from microlayered films.
- Prototype capacitors are being fabricated with a CLiPS microlayered film that has substantially higher energy density than films currently in use.
- Films with a controlled gradient in the layer thickness distribution were successfully processed.
- The 2008 CLiPS Industrial Showcase attracted 51 attendees representing 26 companies or external organizations.
- A new diversity hire in polymer chemistry at Fisk will play a key role in research and education activities for CLiPS.
- An education research partnership was developed with Kent State University to study the Polymer Envoys Program.

**Leadership and Management**

The CLiPS organization and operation plan enable 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 continued to evolve during the past year as summarized in the Organizational Plan (see also Appendix B). In April, Anne Hiltner replaced Eric Baer as Director, thus resuming the role she had taken through the proposal and start-up stages of the Center. Eric Baer resumes the position of Co-Director.
The Director, Anne Hiltner, is the Herbert Henry Dow Professor of Science and Engineering. She 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 the Co-Director and the Executive Committee, the Director identifies measures for evaluating success in both research and education, and defines indicators of success of the program.

The Co-Director, Eric Baer, is the Leonard Case Professor. He partners with the Director in the strategic planning process, in setting research priorities, in identifying and mentoring new faculty, in negotiating fiscal issues with the university, and in other aspects as identified by the Director. He leads the industrial outreach and spinoff activities of the Center. He also pioneered the layer-multiplying technology and leads Platform I.

The management team includes Dr. LaRuth McAfee who serves CLiPS as Executive Director for Education. She is a full-time staff member who leads in planning, implementation, assessment and innovation of the integrated research and education programs. Melani Joseph is a new appointment with the position of Associate Director for Education and Diversity. She serves part-time with responsibilities for special programs and other assignments as determined by the Executive Director for Education. Pam Glover serves as the Executive Director for Operations for CLiPS. She is a full-time staff member who assists the Director in day-to-day management of CLiPS and takes leadership in certain aspects as delegated by the Director. Pam Cook is the Associate Director for Education and Diversity at the University of Texas Austin where she is committed half-time to CLiPS education and outreach programs at UT.

Dr. Charles Bush serves as the Director of Development. 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. His time commitment was increased in February of 2009 by fifty percent to meet the growth in development opportunities from CLiPS research results.

The first CLiPS faculty hire at Case, which targeted members of underrepresented minorities, was hired. Dr. LaShanda Korley joined the faculty of Macromolecular Science and Engineering on July 1, 2007. In the past year, two additional CLiPS faculty hires at Case have been made. Dr. Lei Zhu joined the faculty of Macromolecular Science and Engineering in January, 2009. Dr. John Maia will join the faculty of Macromolecular Science and Engineering on July 1, 2009. In addition, Dr. Chris Ellison, a new faculty hire in Chemical Engineering at the University of Texas, has joined CLiPS. Furthermore, Fisk has identified a diversity faculty hire in Chemistry with expertise in polymer chemistry. This person will be strongly supported and mentored by CLiPS.

The committee structure facilitates effective and efficient operation of the research, education and diversity programs while maintaining close communication and interaction among 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 1-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. Platform meetings are sometimes combined in order to facilitate interactions and coordination among the platforms. The flexibility of web-based meetings greatly facilitates inclusion of faculty and students at the partner institutions.
The education and diversity programs are served by an Education Platform that meets monthly to assist the Executive Director for Education with planning, implementation, translation, and evaluation of the integrated education and outreach programs. The committee membership is drawn from the faculty and staff of the partner institutions and the affiliate colleges and universities.

The Director and Co-Director are assisted by a diverse External Advisory Board. Of the 14-member board, five of the members are African-American, three are women, and one is handicapped. 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. The EAB meets twice a year with the spring CLiPS Annual Meeting and the fall Industrial Showcase Meeting.

The Center interfaces with industry through the CLiPS Investors. To qualify as a CLiPS Investor, a company makes cash contributions of $35,000 annually to CLiPS in the form of a graduate fellowship. Seven companies are currently CLiPS Investors. The CLiPS Investors review the research and education activities of the center in conjunction with the spring Annual Meeting. A broader representation from industry will be invited to the fall Industrial Showcase which will highlight CLiPS research that is covered by provisional patents or is cleared for external presentation.

As part of the research and education mission, the CLiPS Characterization Laboratories have been strengthened. In the past year, we expanded our imaging capability with the purchase of a scanning electron microscope. The X-ray facility was strengthened with the purchase of a new generator which will partially replace the somewhat unreliable rotating anode generator. We also added a far UV-VIS spectrometer. These additions complement the existing comprehensive laboratories for X-ray, AFM, gas transport, thermal analysis, mechanical testing and biaxial orientation. We will continue to make investments in the process laboratory, in dielectric characterization, in the laser and optics laboratories, and elsewhere as needs arise. The instrumental facilities are maintained with the assistance of a laboratory technician.

**Intellectual Merit of the Center**

**Research Vision and Goals**

A broad range of new science and innovation will emerge from the CLiPS unique technology that will be the basis of a global resource for microlayered and nanolayered polymeric materials. The CLiPS research activities will

- 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 and interactions with light.
- Focus the integrated research activities on national priorities of energy, health, environment, and security.

To achieve these goals, the research programs are organized into four research platforms:
- Unique **Enabling Technology** at Case enables fabrication of hierarchical microlayered and nanolayered polymer-based structures and systems. Case plays the leading role in growing this enabling technology.
- Novel **Membranes and Transport Phenomena** exploit the layered hierarchy to achieve unique transport properties. Researchers from UTA, Case, USM, and Fisk collaborate in this thrust under the leadership of UTA.
- Innovative **Optical and Electronic Systems** is based on advanced layered materials. Teams from Case, Fisk, Rose-Hulman, Youngstown State, and NRL collaborate in the development and testing of devices.
- The layer-multiplying process opens new opportunities for **Science and Technology Initiatives**. New knowledge and new properties of microlayered and nanolayered materials are sought.

**Research Highlights and Accomplishments**

**Platform I – Enabling Technology**

Platform I supports a continuous coextrusion process (see picture above) that facilitates creation of microlayered and nanolayered systems by forced assembly of polymers on a size scale as small as molecular dimensions. This flexible, solvent-free technology accommodates the diverse needs of research in Platforms II, III, and IV. The process is user-friendly and students, ranging from high school students to graduate students and research associates, gain hands-on laboratory experience in processing layered systems. During the past year, 4 major processing projects were directed towards maintaining and expanding the enabling technology of Platform I.

(1) Efficient and effective operation of the coextrusion process is key to the continued success toward achieving the CLiPS research Platform goals. Nearly 150 coextrusion trials encompassing coextrusion of more than 75 different polymer materials were accomplished by 3-student coextrusion teams. Fourteen graduate students and one research associate comprise the trained processing teams that operate the co-extrusion process. The teams interact with CLiPS research faculty and students through regular web-based meetings with the partner institutions and weekly processing team reviews.

Multilayered film micro- and nanolayer thickness uniformity achieved with our multiplying die system is adequate for most CLiPS research platform applications, and the process can be scaled up to commercial operation. However, some of the proposed applications, particularly in the optical and electronic materials, continue to challenge us to achieve better film and layer uniformity. Improved multilayer film and layer quality/uniformity were addressed with the acquisition of a new 14” coat-hanger shaped film die and higher quality finishing of film take-off calendaring equipment. These improvements, coupled with the inclusion of sacrificial polymer film surface layers, have produced films with improved uniformity and optical quality surface finishes to meet the high quality standards which are especially important for the Platform III all-plastic laser and reflective optical films. A second surface layer extruder was purchased to enable two different surface layer materials.

(2) Motivated by growing economic trends for rapid evaluation, and production of new and unique cutting edge polymer technology, CLiPS has undertaken material miniaturization modifications to the multilayer coextrusion process. “Miniaturized” multilayered film coextrusion, processing with one
polymer layer composed of approximately 50 grams or less of material, has been accomplished through novel “plug flow” feeding techniques or use of a custom built mini-injection line replacing one extruder. Two recent processing successes of “miniaturized” material coextrusion trials utilized the “plug flow” technique (figure) to directly coextrude and characterize micro-and nanolayered films with one of the layers comprised of: (1) 50 grams of a custom synthesized developmental polymer (Platform IV “Combing Self-Assembly”) and (2) 50 grams of polymer blend layer comprised of a specialty polymer dye (Platform III “3-D Optical Data Storage Films”). The success of these miniaturization “plug feed” coextrusion trials highlights the flexibility of CLiPS’ enabling technology to produce and evaluate highly specialized multilayered films previously unavailable for study based on limited material availability and high costs associated with conventional coextrusion quantity requirements.

(3) CLiPS enabling coextrusion technology continues to provide exciting opportunities for expansion of multilayered polymers to new and exciting frontiers. The design and fabrication of four “uneven” layer multiplying dies with offset split positions in the multiplication die feed channel have enabled successful coextrusion of gradient multilayer films with up to a 10X difference in the thickest and thinnest layers. In contrast to the feedblock approach, the multiplier approach utilized in CLiPS allows for considerable flexibility in the design of gradient layer thickness distributions by varying the multiplying die split ratio and sequencing of a series of “uneven” and conventional even split multiplier dies. Flexibility in the coextrusion of polymer films with different gradient layer thickness distributions may enable production of polymer films with novel optical, transport, and mechanical properties.

Novel optical properties of gradient nanolayered polymer films were investigated by coextrusion through a combination of even and “uneven” layer multiplying dies. A 128 gradient layer PS/THV film with layer thicknesses ranging from 1.2 μm to 110 nm (figure) was coextruded through a series of two conventional and four “uneven” split layer multiplier dies. A wide optical reflection band, measured across the entire 600 nm wide spectrum of visible light, was produced as a result of the large 10X gradient between the thickest and thinnest layers.

Drawing on the flexibility of changing the sequence of “uneven” and even split layer multiplier dies, a 128 gradient layer film exhibiting dual optical reflection peaks was produced by coextrusion through a series of four even and two “uneven” layer multiplying dies. Gradient multilayer films with wide or dual optical reflection peaks have potential applications in the production of special optical filtering and sensory devices. In addition to exploring the large design space for optical effects of unique gradient layer thickness distributions, preliminary work on diffusion and release of dye molecules through a gradient layer film were initiated.
Additional opportunities exist if the layers can be turned around. Converting horizontal layers to vertical layers in our coextrusion line is accomplished by rotating the first multiplier by 90°. Depending upon the number of layers, the vertical layer thickness can be varied from a few microns to millimeters. In the past year, we successfully produced vertically layered structures with millimeter to micron layer thicknesses from a variety of polymers.

A vertically layered system with controlled chemical or physical cross-linking at the layer interfaces can impart unusual mechanical properties in the anisotropic directions. This also makes it possible to measure properties in all the anisotropic directions, which is difficult to do in the thickness directions of the conventional horizontally layered systems. Additional applications of the vertically oriented films and tapes include their use as selective separation membranes for gas mixtures and optical waveguides with reduced refraction. Future research will focus on eliminating or reducing unwanted vertical layer curvature produced during coextrusion. Initial studies to optimize extrusion velocity profiles in layer multiplier dies and exit dies for vertically layered films and tapes are planned. With improved uniformity from vertical layer systems, the effect of the interphase and layer orientation on anisotropic properties of the layered films will be examined.

Platform II – Membranes and Transport Phenomena

Platform II focuses on mass transport phenomena and, more specifically, on membranes and barrier materials. Five multi-investigator research teams were created and are fully staffed. The teams focus on a 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. Layered material systems will be optimized to exhibit transport-property profiles that may be otherwise inaccessible.

(1) Confined Crystallization

Crystallization of polymer chains in a confined space can produce specified crystalline phase orientation. Layer-multiplying coextrusion used forced-assembly to create thousands of alternating layers of two polymers in a continuous process. Each layer can be less than 10 nm in thickness. Coextrusion of a crystallizable polymer into nanolayers confines the polymer chains to the size scale of the lamellar thickness. The anisotropic orientation of crystals in the nanolayers will dramatically affect the film properties, such as mechanical strength and gas barrier.

In the present study, crystalline polyethylene oxide (PEO) was used as the confined layer. Ethylene-co-acrylic acid (EAA) copolymer (9wt% acrylic acid) or polystyrene (PS) was used as the confining layer. The effective PEO layer permeability, \( P_{PEO,\text{eff}} \), in 50 nm layers was 150 times less than \( P_{PEO} \). That is, the confinement effects induced by the nanolayer coextrusion resulted in nearly perfect single crystals of PEO, which had exceptionally high barrier properties. This finding was published in *Science* in February 2009.
Extending this discovery, coextrusion of highly oriented “single-crystal-like” polycaprolactone (PCL) nanolayers was accomplished through layer confinement against amorphous PS layers (figure). A 390X decrease in the multilayer film oxygen permeability was produced as a result of the increased PCL orientation in confined layers similar to the PEO/EAA and PEO/PS system. Further PCL confinement experiments to elucidate material and processing parameters that may affect confined PCL layer structure and properties are planned for the up-coming year.

(2) Low T<sub>g</sub> Glass/Polymer Composites
Low glass transition temperature (T<sub>g</sub>) phosphate glasses (Pglass) that are both water resistant and chemically durable are now available. Their inherently low T<sub>g</sub> make these Pglasses interesting candidates to be melt-processed with general organic polymers, utilizing conventional processing methods such as extrusion and injection molding. With 16 layer extrusion (8 layers of Pglass composite, 8 layers of polymer), 10 volume % Pglass incorporation brings about a 4x reduction in oxygen permeation, achieving 0.1x the barrier of PET. The same composition run into 64 and 128 layers (32 and 64 containing Pglass) results in an about 80x reduction in oxygen permeation vs. the starting PP resin, and an ~2-3x reduction in permeation vs. PET. So, 10% glass in PP under these conditions allows PP to surpass PET barrier to a point similar to that obtained in commercial PET/MXD6 barrier blends used in beer packaging. When the quantity of glass is doubled to 20 volume % of the total film cross section, a 400-500x reduction in oxygen permeability vs. the base resin, and a 10-15x reduction compared to PET is obtained.

(2) Oxygen Scavenging
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. A systematic modeling study was also undertaken as part of this effort, and the first paper from the modeling study has been published.

(3) High Barrier Layered System Containing 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. Three different nanoclays with aspect ratios (L/h) ranging from 27 to 1000 have been selected. Cloisite 20A, montmorillonite (MMT) (L/h = 200) and Laponite<sup>™</sup> RD (L/h = 27) have been purchased from Southern Clay Products (USA). Synthetic Mica (Somasif ME-100, L/h = 1000) was purchased from Co-op Chemical Co. (Japan), and was modified with dimethyl dihydrogenated tallow ammonium chloride (the same surfactant used to make NaMMT into Cloisite 20A) in accordance with established literature procedures. To date, nanocomposite systems containing montmorillonite and synthetic mica have been explored, and excellent dispersion of these nanoclays has been observed, with large improvements in gas barrier properties.

(4) Bio-Inspired Surface Modification to Improve Membrane Fouling
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 will undergo 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. The polydopamine layer also exhibits excellent adhesion properties, as it will not erode even under sonication at extreme acidic conditions. Polydopamine deposition is an easy and effective way to reduce fouling on many industrially-significant water treatment membranes. During this past year, we have found that the polydopamine surface provides a universal platform for further chemical surface modification. Polydopamine- and PEG-modified membranes showed dramatic reductions in protein adhesion over unmodified membranes for all classes of membranes tested. On this basis, a start-up company, Advanced Hydro, Inc., was launched in December 2008 to take advantage of this discovery and reduce it to practice.

(5) Controlled Atmosphere Packaging

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 some 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. This requires identifying materials with higher CO$_2$/O$_2$ selectivity than found in most polymers and then combining these materials into a practical membrane structure using microlayer coextrusion technology. 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. Thus, the immediate challenge is finding ways to incorporate PEO units into structures, such as block copolymers, that exhibit favorable separation properties. A line of thermoplastic elastomers produced by Arkema Inc., known as PEBAX block copolymers, are an attractive option for packaging applications. Previous experience$^{1-3}$ with these materials suggests that they may be suitable for this application. Arkema Inc. generously provided five different grades of PEBAX in pellet form to begin 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.

Platform III - Optic and Electronic Systems

CLiPS’s enabling process technology is uniquely suited to facilitate new science and technology relevant to the broad field of optical and electronic phenomena where multilayer structures represent a common general architecture. Research Platform III seeks to exploit this tremendous opportunity by carefully addressing selected projects in areas of significant national interest through the application of core competencies. Projects are underway to study the interactions of light with micro- and nano-layered polymeric materials with the applications in photonic and optoelectronic devices.
In September, 2008, Platform 3 held a retreat to plan activities for the coming year aimed at producing high impact results for a strong renewal proposal. All projects were discussed and new project topics evaluated. Several changes were made to the project portfolio. The terahertz components project was ended. It was determined that short term high impact results were more likely elsewhere. Both the photovoltaic and nonlinear optics projects were redirected. The nonlinear optics project would be reduced and placed on the “back burner.” The approaches we were pursuing did not seem promising. However, advances in high response, melt-processable molecular materials will be monitored, and if promising new materials were found or reported, we could revisit applications in optical switching a limiting. Efforts in nonlinear optics would emphasize optical data storage in the near future.

The photovoltaic project would continue, but change its emphasis. There was a shortage of promising ideas to fabricate multilayer polymer photovoltaic devices in the short term using the co-extrusion process. Activities would continue in polymer/oxide hybrids, while new efforts in optical coupling to photovoltaic devices were initiated. One approach uses cavity effects to enhance the effective absorption of sunlight.

New projects were initiated. A project to demonstrate 3D optical data storage based on two photon writing would be pursued. This could be a potentially high impact demonstration. Currently, there is considerable interest in multilayer 3D optical storage, but no low-cost production method. The CLiPS project could make an important contribution in demonstrating such a low-cost method. Jie Shan is leading the effort to demonstrate 3D storage in preparation for the renewal proposal.

A new opportunity to make high performance optical filters for art conservation in collaboration with University of Texas, El Paso presented itself, and Jim Andrews will lead that effort. These filters are characterized by several narrow transmission window to accurately render color, while reducing exposure to damage from excessive illumination.

Finally, Youngstown State University will investigate two avenues for seed projects: multilayer films for magneto optics, and microfabrication in two dimensions to make 3D structure. Magneto optics is currently a topic of high interest to the military to in optical communication as magneto optic devices can be used to minimize laser back reflections as optical isolators. Mike Crescimanno at YSU will work with Jim Andrews on theoretical and experimental work to demonstrate enhanced Faraday effects in multilayer films. It is believed that regions of enhanced density of photon states will strengthen the response. Tom Oder at YSU will work with Anne Hiltner on microfabrication in multilayer polymer films.
The first target will be microlens arrays.

(1) Research has continued to investigate Light Emission and All-Polymer Lasers. Students under the supervision of Profs. Singer, Andrews, Baer, Hiltner, and Weder are participating in this project. Two structures including microcavity lasers using distributed Bragg reflectors (DBR) fabricated from multilayer films, as well as distributed feedback lasers (DFB) have been designed, built and tested. An extensive study of DBR lasers including both a commercial and center-synthesized OPV dye has been completed. Major results indicate high efficiency, low threshold lasers. Lasers with rhodamine 6G dyes exhibit thresholds using a nanosecond pump laser as low as 160 μJ/cm2 and efficiencies near 15%. The output of one such laser shown in the accompanying figure showing a very bright well-defined spatial mode emission. The emission also exhibits spectrally narrow multi-longitudinal modes. Our publication on distributed Bragg reflector lasers in *Optics Express* garnered significant attention in trade literature with stories written in *Laser Focus World* and *optics.org*. In addition, the work was chosen as a research highlight of 2008 in *Optics and Photonics News*. The highlights are highly selective. A provisional patent has been filed. In addition, we have demonstrated high efficiency, low-threshold lasing in distributed feedback laser structures. A manuscript is in review. Research into upconversion lasers, new laser dyes and gain media, and tunable lasers is in progress. A graphical user interface computer application for optical design of multilayer films is under development.

(2). A new project in Optical Data Storage was initiated. The multilayer polymer process could be a revolutionary method for low-cost production of 3-D optical data storage based on multilayer writing of data. Schemes to do this are currently receiving considerable attention, but commercial implementation is hampered by high costs. CLiPS recognizes an important opportunity here. The scheme involves alternating spacing layers with active data layers. Writing would be limited to individual layers by using two-photon writing processes which confines writing to the focal volume. Reading would be done with confocal microscopy. Our challenge in this first year of this project is to identify credible writing schemes that are compatible with the melt process. We have identified two promising schemes using a two-photon absorbing dye and the heat produced on two-photon absorption to (1) crystallize the polymer host and (2) to form dye aggregates with excimer emission properties. Multilayer films are being processed and demonstration experiments are planned in the near future.

(3) The Multilayer Optics project has several components including Gradient Refractive Index (GRIN) Optics led at Rose-Hulman, a project in collaboration with University of Texas El Paso (UTEP) to design and fabricate high performance color filters for art preservation, and a project to design methods for efficient optical coupling into photovoltaic devices. For GRIN optics, work has focused on polymethyl methacrylate (PMMA) and styrene acrylonitrile (SAN17) layered structures that can have a variable refractive index in the range of 1.49 to 1.57. Beam shaping applications are receiving attention since they could play an important role in illumination, laser cutting, and solar energy collection. The connection between all of these applications is the desire to redistribute the energy of the beam into a shape that maximizes the desired effect with little to no loss. Axial GRIN lenses have been fabricated and tested, and have been shown to have high image contrast and other promising optical characteristics. In addition, modeling has shown that high quality GRIN optics could be feasible using few layer steps leading to lower cost manufacturing. Progress on GRIN prism and spherical GRIN lenses is reported. Intellectual property protection is now being pursued in the area of GRIN optics. Multilayer optics design software is being used by CLiPS scientists and Prof. Dirk at UTEP to design new thin film color filters that accurately render the colors in works of art with the minimum illumination at wavelengths known to degrade art works, and for minimal illumination. Implementation of these filters in multilayer films is being investigated. Finally, new concepts in cavity effects for efficient coupling into photovoltaic cells are being investigated by CLiPS faculty at CWRU and Fisk. This approach could have a substantial impact on high-efficiency low cost polymer photovoltaics.

(4) The Nonlinear Optics project has been scaled back but work continues in characterizing new chromophores for nonlinear optics using z-scan. This work aims to develop a better understanding of
nonlinear optical (NLO) properties in multilayered polymer systems for ultimate use in optoelectronic applications. Components of this study are theoretical modeling and numerical simulation, design and synthesis of novel materials, linear and nonlinear optical measurements and development of the multilayer processing for optical materials. Notably, a new melt-processable squaraine dye has shown an exceptional nonlinear optical response and will be investigated in thin film form in the near future.

(5) New seed projects were initiated at Youngstown State University. In one project, multilayer structures for Faraday and surface magneto-optic Kerr effect rotation are being investigated. In particular, surface and band edge enhancement effects for optical modulation and optical isolation are the focus of this work. Modeling and experiments are underway. Numerous potential applications of functionalized multilayer polymer materials depend not only on the layering of the material, but also on the ability to pattern the resulting structure laterally. Microlens fabrication is being developed.

Platform IV – Science and Technology Initiatives

An additional 6 projects explore new opportunities to understand and exploit the micro and nanolayered systems. As they evolve, it is anticipated that some these projects will naturally fit into one of the existing platforms. Others will be the seeds for new platforms. It is also anticipated that, because these are the higher risk projects, some will not be successful. Indeed, a project on photopatterning multilayered films has been on hold until a method is found for preventing diffusion of low molecular weight dyes.

(1) Homogeneous Nucleation

Breakup of polymer nanolayers into submicron droplets is a novel approach for studying crystal nucleation. Nanolayers of polypropylene (PP) separated by thicker microlayers of polystyrene are co-extruded. Breakup of the 12 nm PP nanolayers during heating results in primarily submicron droplets, dispersed in a polystyrene matrix. The submicron droplets crystallize at 40°C, which is identified with homogeneous nucleation of the particles in the meso-form. Most of the droplets obtained were in a size range of 100-1000nm. The granular morphology of smectic PP was observed in the droplets crystallized at 40°C where most of the grains were in a size range 15-30nm. The formation of the smectic phase showed unusually slow kinetics. During heating, the smectic phase transforms into monoclinic alpha form. This structural transformation was studied by annealing the droplets at various temperatures. The morphological features showed a little change in the grain size. However, strong alpha reflections were observed in WAXS suggesting the internal rearrangement of smectic chains into an ordered structure. Based on our results we will propose a scheme for formation of mesophase and the structural transformation of meso to alpha phase on heating. Manuscript writing for this study is in progress.

Exclusive homogeneous nucleation of PP droplets offered a unique opportunity to probe nature of heterogeneous nucleation by adding various nucleating agents to PP nanolayers. Initial studies that focused on nucleation of the α-form by Millad, which is soluble in PP melt. In our earlier work, we had proposed three regimes of Millad nucleation. We have now studied the unique morphological features of Millad nucleated droplets in these regimes. This approach has been extended to study β-form nucleating agent, Quinacridonequinone (QQ). The morphology studies have shown that QQ nucleated PP in the alpha form in addition to the β crystal form (Figure).

In collaboration with Galeski and Piorkowska at the Polish Academy of Sciences in Lotz, we are studying the crystallization of HDPE and PP droplets under conditions of high temperature and high pressure.
where the polymers crystallize in different crystal forms. An important result is that nucleation, presumably heterogeneous, is necessary and advantageous for the formation of the HDPE pseudo-hexagonal phase or the polypropylene orthorhombic form. The first manuscript was published Macromolecules and a second is in preparation.

(2) Self-Assembly at the Layer Interface

The potential for reactions at the interphase is being exploited by Rowan with focus on the study of self-assembly by means of metal-ligand interactions. We have successfully accomplished the synthesis of two different telechelic polymers with metal-binding end-groups. The macromonomers were synthesized on a 10-15 gram scale for microlayering. Encouraged by the success of the first multilayer experiment, a new self-assembling system has been developed that should improve upon the current system. One of the major issues with the previous design is that in order for high molecular weight supramolecular polymer to result at the interface, a strict ratio of 1:1 metal ion to macromonomer needs to be present there. If, as is likely this turns out not to be the case, then self-assembly will still result but only oligomers will be formed. One way round this issue is to design the macromonomers with more than two ligands per polymer chain. As long as at least two of the ligands are bound, high molecular weight network aggregates will result.

The same general self-assembling scheme (metal-ligand) as the previous system is employed. However, the design on the macromonomer is significantly different. For this, low molecular weight oligomers of side-chain functionalized polystyrene are being investigated as a means of studying self-assembly occurring within multilayers. Synthesis of a multi-functional side-chain functionalized polystyrene has been achieved through the use of a living polymerization. The initiator used to accomplish this is synthesized by combining styrene, benzoyl peroxide (BPO) and TEMPO and heating to 80 °C for 20 hrs. An excess of TEMPO is used to act as a radical trap, ensuring that the initiator is formed without polymerization. The yield of the initiator synthesis is low, but as it uses readily available reagents the reaction has been carried out on gram scales.

(3) Physical Aging in Confined Layers

In recent years, studies have shown that thin, free-standing polymer films (<1 μm in thickness) undergo physical aging much more rapidly than thicker “bulk” films. It is thought that the short relaxation times of the surface material are responsible for the rapid aging. It may be possible to modify these surface effects if the thin film is constrained in microlayer films.

The effect of the constraint on aging of thin films of an amorphous polymer is being studied by Paul and Freeman at UT and Baer at Case. Several successful microlayer co-extrusions of polysulfone (PSF) and an ethylene-octene copolymer (EO) were made. The normalized oxygen permeability seems to indicate that the layered films are aging in a manner similar to the bulk films. A 400 nm free-standing film exhibits much more rapid aging than that observed so far for any of the layered films currently being explored. We are presently augmenting the diffusion measurements with thermal analysis, which is conventionally used to characterize physical aging of polymers. We also plan to see if and how the confining polymer affects the rate of physical aging.

(4) Combining Self-Assembly with Forced Assembly

The research plan merges self-assembly with forced-assembly to determine the effect of confinement of block copolymers on thermo/mechanical properties of multilayered systems. Through the study of these properties, we foresee gaining insight into the morphological changes that occur as the layer thickness reaches that of the block copolymer domain spacing. The enabling technology of multilayer co-extrusion provides a unique approach to better understand the effects of interfacial adhesion, interphase regions, and changes in morphology on the material properties of multilayered systems.
Nanolayer films of a hydrogenated block copolymer, Kraton G 1730, are confined against polystyrene layers through the co-extrusion process. Current microlayer runs have produced films with up to 1024 layers where the individual block copolymer layer thicknesses ranged from 620 to 12 nanometer. This range of compositions and layer thicknesses enables a systematic study of the role of confinement via forced assembly on the thermal and mechanical behavior of PS/Kraton multilayered films.

Initial stress/strain measurements show an increase in ductility as the Kraton layer thickness decreases with the mode of deformation changing from crazing to shear yielding. Using DMA and tensile deformation, we are continuing to probe the microdeformation mechanisms in order to understand the transition to ductility. Mechanical models of composite systems, such as Series and Kerner, will be utilized to predict the critical factor involved in the variations in the deformation mechanics of the confined multilayer systems. The morphology within the multilayer films of the BCP will continue to be investigated through AFM and SAXS. Other block copolymers will be coextruded as microlayers in order to test the findings with the initial block copolymer.

(5) Microlayered Dielectric Materials

A focus on novel dielectric materials fabricated with the microlayer coextrusion process is a collaboration among Baer, Zhu and Hiltner at Case, Shirk at the Naval Research Laboratory and Flandin at the University of Savoie. This project is also aligned with the Case-wide initiatives in energy.

There is a need in electronic systems and pulsed power applications for capacitors with high energy density and low loss. From a material standpoint, energy density is proportional to the dielectric constant times the breakdown strength squared. Current state-of-the-art materials are, however, limited in that a tradeoff generally exists between the two properties. Our approach to improve capacitors is to combine, through microlayer coextrusion, two polymers with complimentary properties: one with a high dielectric constant (polyvinylidene fluoride based polymer) and one with a high breakdown strength (PP, PC, PET, or PEN). With this approach, we produced layered dielectric films with more than double the energy density (13 J/cm$^3$) of BOPP while maintaining a low loss (Figure). These films are now being fabricated into prototype capacitors.

In contrast to the monolith controls, multilayered films with various numbers of layers and compositions exhibited treeing patterns that hindered the breakdown process. Thus, substantially enhanced breakdown strengths were measured in the multilayered films. Based on the acquired data from the PC/PVDF-HFP system, a breakdown mechanism similar to the “barrier effect” was formulated to explain the increased dielectric strengths. A manuscript reporting this exciting result has been submitted for publication.

We have extended this work using other PVDF based polymers and insulating materials. The PVDF based polymers included PVDF homopolymer, PVDF-TFE, and PVDF-HFP with various HFP

![AFM image of PS/Kraton G 1730. The nominal Kraton layer thickness is 400 nm.](image)
comonomer contents. The insulating materials included PC, PP, PET, and PEN. These improvements in breakdown strength from microlayering have also been increased an additional 10-15% by biaxially stretching the extruded films.

In addition, a substantial reduction of polarization hysteresis arose from layer confinement effects (Figure). This is very desirable because lower hysteresis results in higher efficiency and less dielectric nonlinearity. The polymer morphology has been studied as a function of layer thickness to search for a relationship between polymer structure and dielectric hysteresis.

In the future, the layer confinement effect on hysteresis will be further probed. In addition, several new materials will be scouted to further increase the energy density and operating temperature; these include high Tg polycarbonate and polysulfone. The energy storage properties of the biaxially oriented PET/PVDF-HFP and PEN/PVDF-HFP systems will also be measured.

(6) Effect of Confinement on Mechanical Behavior

The effect of confined PEO crystallization on the mechanical properties of microlayered and nanolayered films is being investigated. Stimulated by the dramatic effect of confined crystallization on the polymer morphology, we have undertaken a complementary study of the mechanical properties.

We found that EAA/PEO films retain the ductility of the EAA component although the PEO is very brittle. Decreasing the layer thickness of 50/50 films resulted in a substantial increase in the modulus and a significant reduction in the glass transition intensities of both materials (Figure). Our previous study recently published in Science shows that the crystalline lamellae of the PEO become more aligned as the layer thickness decreases, transitioning from a spherulitic morphology to single crystals. We hypothesized that as the PEO layers become thinner, an increasing fraction of the load is carried by the oriented PEO crystals. To test this hypothesis, a mechanics approach was developed to correlate the changes in mechanical properties to the morphological changes. The simple model utilized a combination of the standard linear solid model and the Takayanagi 2-phase model. The model quantitatively described the decrease in glass transition temperature. We demonstrated that the reduction in glass transition intensity is not due to changes in mobility of the polymer chains, as much literature has suggested of amorphous polymers. A manuscript reporting these results is in preparation.
Integration of Research and Education

Vision and Goals

CLiPS’ 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 successful 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 group of American students from middle school through the PhD level.

In order to achieve these goals, the program objectives are to

- Design and implement new graduate courses in polymers, develop advanced modular graduate courses in “polymers plus”, and create polymer courses for Fisk and Affiliates
- Build a supportive environment for polymer research and teaching at all CLiPS institutions
- Foster undergraduate research experiences in polymer science and engineering
- Excite and encourage students at a young age through hands-on research in polymer science and engineering
- Engage the broader community in polymer science and engineering through CLiPS research and education programs

Evaluation tools have been developed for all initiatives to determine their success. Partnerships with the Kent State University Research and Evaluation Bureau and UT Dana Center are allowing for formal education research on key programs to occur.

Course and Curriculum Development

The interdisciplinary nature of CLiPS engages students from different academic disciplines in the “polymers plus” concept. Recognizing a broader need to provide graduate students with a common basic level of understanding in polymer science and engineering, the Case Department of Macromolecular Science and Engineering was motivated to perform a comprehensive evaluation of its graduate curriculum, a process that had not been seriously attempted in over twenty years.

Four new “Foundation Courses” were designed, which bring students to the same knowledge level in the core areas of polymer science and engineering. Integrated into these courses are laboratory and term paper components, which directly relate to what is being taught in classes. Additionally, a series of modular courses provide the student options to go into more depth in specific polymer areas. The new curriculum was introduced in Fall 2007 and has shown positive results in evaluations to date. CLiPS faculty members are involved in all aspects of teaching these new courses and the Center supports evaluations as requested.

In addition to supporting the revised curriculum, CLiPS at Case sponsors seminars featuring polymer researchers in CLiPS-related areas. These are organized as part of the colloquium in the Case Department of Macromolecular Science and Engineering, so students and faculty outside of CLiPS are exposed to these topics. The two CLiPS seminars in Year 3 were designated as CLiPS-ACES seminars (ACES is the Case NSF ADVANCE) to focus on the impact of female polymer researchers. In addition to the technical seminar and meetings with researchers, CLiPS-ACES speakers participate in a university-wide event while they are on campus.

To support CLiPS’ goal to develop the future leaders in the polymer science and engineering community, CLiPS sponsors professional development seminars for graduate students. To this end, The University of Texas offers technical writing seminars for students who feel they need guidance in that area. At Case, graduate students who mentor younger students have expressed an interest in learning techniques for becoming better mentors. To support these students, CLiPS hosts a mentoring seminar series that discusses best practices in mentoring. In addition to learning proper mentoring techniques, this seminar
series allows for the development of a network of mentors who can support each other through issues that arise with their mentees. Feedback from previous offerings of this series was highly positive.

Affiliate Institutions

The main focus for the Affiliate Institutions is to expose and involve undergraduate students in CLiPS research and teaching. These are primarily undergraduate institutions in the geographic region surrounding Case. The current Affiliates are Ohio Northern University, Rochester Institute of Technology, Rose-Hulman Institute of Technology, the State University of New York at Fredonia, and Youngstown State University. Additionally, in Year 3 North Carolina Agricultural and Technical State University joined CLiPS as an Affiliate. Their activities will focus on education efforts in the Chemical Engineering Department and materials research in the Civil Engineering Department. In consultation with the CLiPS Executive Director for Education and researchers at Partner Institutions, each institution prepares an annual statement of work for CLiPS.

All Affiliate Institutions are expected to develop education and research activities. One example of educational contributions by Affiliates is a planetarium-based project currently in development. This activity is a collaboration between Case, Fredonia, and YSU, where the planetarium is located. Fredonia has developed CLiPS videos in Years 1 and 2 that are being modified for the all-dome video format in the YSU planetarium. Case is additionally developing posters and activities for pre-college schools that will be integrated into the all-dome video project. On the research side, Rose-Hulman has become very involved in CLiPS Platform III research. Their activities have been presented at a number of conferences and preliminary disclosures have been made as a first step to patent some of their developments. These are just two examples of the many highly successful results that have come out of the Affiliate Institutions.

Undergraduate Research & Conferences

The Summer Undergraduate Research Internship (SURI) program is a cornerstone of CLiPS’ efforts to introduce CLiPS technologies, polymer science, and more broadly research in STEM disciplines to a diverse group of American students. This program enables a group of students to conduct research in an intensive manner for 10 weeks each summer on the Case campus. Students work as members of CLiPS research groups, under the mentorship of a PhD student or Research Associate. In addition to daily research activities, SURI students also participate in weekly program meetings during which they present their results to one another, in addition to receiving lectures on areas of polymer science and engineering ethics. SURI culminates with the Northeast Ohio Undergraduate Polymer Symposium, which brings together summer students from Case, the University of Akron, Kent State University, and the NASA Glenn Research Center. In Summer 2009, the Case SURI program will host ten students from Fisk University and/or Affiliate Institutions. In this way, CLiPS supports students at Center institutions and encourages them toward careers in polymer science and engineering. They, in turn, will take this knowledge and enthusiasm back to their campus.

The broad participation of American undergraduate students in STEM-related research careers is an overarching goal of CLiPS. To this end, research conferences that bring together such undergraduates are an important venue from which to both advertise CLiPS technologies (increasing the eventual PhD candidate pool) as well as broadly increasing the level of interest and excitement about these career options. Beginning in Fall 2007, CLiPS co-hosted the INSPIRE conference, a national conference for undergraduate polymer researchers. This conference will be hosted again in Spring 2010. In Year 4 of CLiPS, an Affiliate Institution research conference is additionally being developed to showcase the undergraduate research taking place within CLiPS.
In the previous reporting period CLiPS additionally started organizing symposia at local and national conferences. UT researchers hosted the ICOM conference in July 2008 that brought together membrane researchers and allowed CLiPS activities to be showcased. Additionally, Case faculty and staff are actively working to organize functional materials and education symposia at the 2009 ACS Central Regional Meeting and the 2009 AIChE Annual Meeting.

Polymer Envoys Program & Pre-College Initiatives

In addition to exposing current college students to polymer science and engineering, CLiPS endeavors to excite and encourage students at a young age to consider such fields. To this end, the Center institutions are developing educational initiatives for pre-college students, especially those in middle school and high school. At Case, relationships have been developed and strengthened with the Cleveland Metropolitan School District (CMSD), allowing pre-college students to participate in CLiPS research under the supervision of a graduate student and part of a layered research team. This initiative with the CMSD is called the Polymer Envoys Program (PEP) and it is also one of the Center’s two primary diversity initiatives. Case has daily responsibilities for activities within PEP, including financial support of the participating students and teachers. Case has hosted 19 students to date, and will have 7 incoming students in Fall 2009. The PEP model has been translated to the CLiPS partners and, after assessment, will be translated to the nation. To this end, within CLiPS UT (W07), RIT (Su07), Fisk (F08), and Rose-Hulman (F08) have also developed PEP sites with their local high schools. UT has sponsored 7 students in their program and RIT, Fisk, and Rose-Hulman have hosted two each.

While not essential to success, one goal of the pre-college initiatives is to encourage the participants to attend college at a CLiPS Institution. The UT program has had three students graduate thus far, with one at UT majoring in a non-STEM field and the other two at other UT campuses in STEM fields. One of these students at another campus intends to transfer to the Austin campus later in his college career. At Case, two students in the class of 2008 matriculated at Case in Fall 2008, and both are majoring in Polymer Science & engineering. In agreement with a previous university commitment, the Case Provost’s Office and Case Alumni Association have pledged funds to cover the majority of these students’ college expenses.

The CMSD has developed parallel activities for PEP students and teachers. These parallel activities include support for the PEP students to present polymer demonstrations in science classes for younger students and support for teachers to participate in program-related professional development activities. The CMSD works closely with Case to ensure that these efforts stay aligned throughout the duration of the initiatives.

Recognizing the importance of reaching the greater community, PEP events are used to share polymer information with the families and friends of the participating students. Each Case participant is required to bring at least one parent to the Welcome Meeting where the goals of the program are described, and parents are encouraged to attend the poster sessions at which students present their projects.

In addition to PEP activities, CLiPS hosts a range of formal and informal pre-college programs that reach hundreds of students annually. At Fisk, a Middle School Science Club and Saturday Science Academy for high school students allow CLiPS to interact with ~80 students for monthly activities. Likewise, UT sponsors
monthly activities at the Austin Children’s Museum to promote science and engineering to visiting students and their families. Finally, Case hosted a one-day event in Fall 2008 that brought 8th grade students from local schools to campus, with the goal of exposing them to science and engineering opportunities. Case recently hired an Associate Director for Education and Diversity who is developing additional pre-college programs with Cleveland-area schools and organizations.

General Education Outreach

Case also participates in general outreach activities directed toward the campus and local organizations. One example of a recent event is CLiPS participation in the annual Research ShowCASE in April 2009. CLiPS had a booth at the event that featured a general poster on the Center and examples of the materials produced. Additionally, CLiPS graduate student researchers presented posters on their projects, and four of these posters received awards. Research ShowCASE is open to the entire Case campus and local community, so people who visited expressed interest in both the research and educational activities in the Center.

Integration of Diversity into CLiPS Programs, Projects and Activities

Diversity Vision and Overall Goal

CLiPS’ overall goal for diversity is 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. The two main diversity initiatives are

- The Case-Fisk Alliance, which involves pre-college students through faculty
- The Polymer Envoys Program, which is geared toward high school and middle school students

The overall goals and objectives for these initiatives have not changed since the CLiPS Year 1 Strategic Plan. However, some intermediate plans and deadlines have been modified. Since PEP was described in the Education section of the Context Statement, it will not be described in this section.

Case-Fisk Alliance & MSI Initiatives

The primary goal of the Case-Fisk Alliance is to serve as a compelling national model for fully-integrated, broad interactions between Minority-Serving Institutions and Research Universities to broaden participation in STEM fields. The Case-Fisk Alliance will be a vehicle for research accomplishments in the areas of electro-optical systems and glasses, and diversity in human resource development within the STEM fields. This integration of Fisk as a full research and education partner in CLiPS is the main objective to be accomplished through the Case-Fisk Alliance.

The partnership between Case Western Reserve University and Fisk University encompasses educational initiatives ranging from the faculty level to the high school student level. Some of these activities include joint student and faculty recruitment, internship programs, and new courses. Having this type of partnership allows for mentorship of junior faculty by senior faculty on either campus. Additionally, it exposes graduate student and postdoctoral researchers to research and professional opportunities on each campus. This is a rare complete research and educational partnership between a research university and a minority-serving institution. Within CLiPS, the University of Texas is developing a similar relationship with the University of Texas – Pan American, and significant collaborative activities began in Summer
2008. This connection with UT-Pan American is also leading UT to develop a collaboration with UT-Brownsville.

Fisk undergraduate students can choose to participate in a recently developed binary program offered through the Case School of Engineering and Fisk Division of Natural Sciences and Mathematics, and encouraged by the Case-Fisk Alliance. This allows students who begin their undergraduate science coursework at Fisk to easily transfer to Case and obtain a BS in an engineering discipline. Fisk students also have the opportunity to participate in summer research at Case through the CLiPS SURI program, and two Fisk students will be at Case this summer in this program. Undergraduate students who participate in these and other Case-Fisk Alliance initiatives are encouraged to apply to Case and/or Fisk for graduate school. Faculty at each institution work to facilitate the admissions process for students who do apply. For example, a Fisk MS alumnus who spent Summer 2008 doing research at Case will matriculate into Case Materials Science and Engineering PhD program in Fall 2009. This student’s successful experience with summer research at Case as a graduate student will become the model for future expectations of Fisk graduate students in CLiPS. Students at Fisk will now be designated as CLiPS Scholars when they begin graduate school and they will be expected to spend a summer at Case or UT to participate in research with partner researchers. A similar structure has been used between Fisk and Vanderbilt, and has caused many Fisk alumni to matriculate in doctoral programs at Vanderbilt.

In addition to restructuring the graduate student expectations, CLiPS is excited that Fisk is finalizing its polymer chemistry faculty search process. This new faculty member will play a key role in research and education activities for CLiPS at Case and it is expected that the candidate will begin in June 2009. Since the current candidate will initially develop stronger research collaborations with UT, the Case-Fisk Alliance is being expanded to include UT. To recognize this broadened connection to Center institutions, the initiative will now be called CLiPS @ Fisk.
Partnerships and Knowledge Transfer

Knowledge Transfer Vision and Goals

The goal set forth for the Center regarding knowledge transfer is to be a unique global resource for the dissemination of knowledge in the area of layered polymeric systems. The goals are facilitated through a high-tech communications infrastructure within the Center and a separate web site which serves as a resource for information to the external world.

The knowledge transfer programs are accomplished through the following:

- Symposia to review Center activities with faculty, students, the CLiPS External Advisory Board and CLiPS industrial investors
- Symposia to disseminate, extend and communicate information about CLiPS research and educational programs with faculty members, students and the academic and related industrial community
- On-going productivity as evidenced by presentations at conferences and workshops, and scholarly publications
- Maintenance and updating of the CLiPS website on an on-going basis to disseminate information within and beyond the Center

Center Meetings

Fulfilling the objective of organizing symposia that focus on reviewing the Center’s activities for and with its members, the following activities were undertaken:

- CLiPS Annual Center Meeting – March 12, 2009 in Austin, TX. This meeting is a bringing together of all stakeholders in the Center to review, evaluate and plan for the upcoming year. This year the meeting included faculty, staff, and students from all participating institutions, the External Advisory Board, and the CLiPS Investors.
- CLiPS Investors Meeting – March 11, 2009. An in-depth, interactive meeting with representatives of the Center’s industrial investors regarding the progress and direction of the research projects with which they are involved.
- External Advisory Board Meetings – October 22, 2008 and March 12, 2009. A twice yearly meeting 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.

CLiPS Annual Meeting – March 12, 2009

[Images of participants at the CLiPS Annual Meeting]
Symposia
Symposia that were designed to communicate information about the Center to a wider audience included:

- **CLiPS Industrial Showcase**
  
  This important new symposium which was held in the fall of 2008 presented CLiPS research and technologies to a broad cross-section of industrial and other external organizations. It is planned to repeat this event every two years. Industrial companies that represent a logical fit for current or potential CLiPS research were invited to this event. The meeting tested the interest of industrial partners as potential investors and/or collaborators in current CLiPS research projects, and served to accelerate the process of developing intellectual property, spinning off projects to industry, and creating new businesses.

  The 2008 Industrial Showcase had 51 attendees representing 26 companies or external organizations. Two of the attendees (Proctor & Gamble and Daikin) became CLiPS Investors and several others are engaged in discussions regarding further research and commercial exploitation of specific technology areas within the center.

- **CLiPS Sponsored Seminars – October 24, and November 14, 2008.** As part of the Department of Macromolecular Science and Engineering Seminar series, and in conjunction with the ACES program (Case’s NSF ADVANCE Program), CLiPS sponsors two seminars each year featuring speakers who are women engaged in polymer research. The audience for the seminars includes faculty, staff and students in the department, as well as other interested individuals.

Research and Academic Productivity
The Center’s research and academic productivity as evidenced by peer-reviewed publications and presentations has continued to enjoy dynamic growth over the past year:

- Center faculty members and students published twenty-six papers in peer reviewed journals, two book chapters, and five additional papers in non-peer reviewed journals. Many of these publications represent the collaborative effort of researchers from across the Center.
- Center faculty members gave twenty-three research presentations
- Center staff members gave two educational presentations
- Students and post-doctoral associates accounted for an additional forty-five research presentations.

Another highlight in the area of research productivity involves submission of four provisional patents applications with four more applications in process. These are listed in the following table:

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<th>Status</th>
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<td>Applied For</td>
<td>Glass-containing high barrier films.</td>
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<td>Applied For</td>
<td>Polymer multilayer dielectric films.</td>
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<td>Applied For</td>
<td>Low cost, tunable, polymer laser.</td>
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<td>Multilayer polymer barrier films.</td>
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<td>Laser Beam Shaping Device</td>
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<td>Improved Permeability Biaxially Oriented Polypropylene Films</td>
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<td>Gradient Layer Films</td>
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<td>In process</td>
<td>Photovoltaic Optical Cavity technology</td>
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CLiPS Web Site
The CLiPS web site continues to be visited often by industrial representatives and academicians from the US and abroad, by potential students searching for information about CLiPS programs, as well as by CLiPS participants. As the Center evolves, updates are made to the website to reflect those changes. In the year between April 14, 2008 and April 14, 2009, the CLiPS web site had over 3500 visitors (up from 1000 visitors the year before.)

Value-Added of CLiPS
A very exciting new 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 economical 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. Fabrication of hierarchical microlayered and nanolayered polymer-based structures and systems is addressed in Platform I. This flexible, solvent-free technology accommodates the diverse needs of Platforms II, III, and IV. Fundamental science and technological applications, such as membranes and optical/electronic systems, are addressed in Platforms II, III and IV. The broad scope of the research activities requires participation of outstanding researchers and educators in many disciplines, including polymers, optics, electronics, material science, and transport. To meet this challenge, CLiPS has assembled a multidisciplinary, multi-institutional team of investigators. The knowledge transfer program 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, faculty and associated researchers. Emphasis is placed on teamwork, communication and engagement of students at all levels in research and education activities to make CLiPS a unique place for training 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 aims to capture the features of modern US society with an emphasis on teamwork, communication, and workforce diversity, in addition to excellence in research and education.

CLiPS Removes Boundaries
- Students: high school/undergraduate/graduate
- Faculty: secondary/college/university
- Educational Institutions: non-PhD-granting schools/HBCUs/research universities
- Focus Activities: science/technology/application

Not Possible with a Single Investigator/Institution