2. 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 (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 Eric Baer, and the Co-Director, Professor Anne Hiltner. The strategic plan for achieving the CLiPS vision is distilled with the assistance of a diverse External Advisory Board.

CLiPS Partner Institutions

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 full 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 UT, RIT, and Fisk 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 <u>Enabling Technology</u> 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 2007-2008

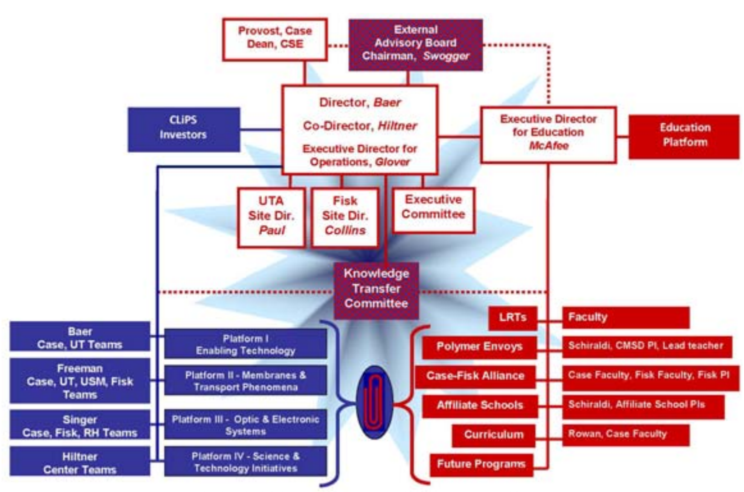
- Films with a gradient in the layer thickness distribution were successfully processed
- An all plastic laser with low threshold and high efficiency was fabricated from microlayered films
- Two graduating CLiPS Envoys will enroll as Case freshmen in the fall
- An African American graduate from Fisk enrolled in the PhD program at Case
- Professor Hiltner received the ACS Award in Applied Polymer Science at the 2008 spring meeting
- Dr. Charles Bush joined CLiPS to promote technology transfer activities

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 and the result is described in the figure. The **Director** is Eric Baer. He replaces Anne Hiltner, who now serves as the **Co-Director**. Dr Baer is the Leonard Case Professor of Engineering. He pioneered the layer-multiplying technology, served as CLiPS Research Chair during the startup phase and leads Platform I.



CLiPS Management Organization

The Director is a faculty member who 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 in year-4 of the program.

The Co-Director, Anne Hiltner, is the Herbert Henry Dow Professor of Science and Engineering. Dr. Hiltner led the CLiPS startup phases. As Co-Director, she will partner 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. She oversees the CLiPS budget, manages the CLiPS Laboratories, and serves as Platform IV leader.

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. Pam Glover serves as 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. Dr. Charles Bush recently joined the management team at Case as a consultant to coordinate the intellectual property and industrial outreach activities of the center. Pam Cook is the Assistant 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. S. Ray Bullock joined the Fisk team and is committed half-time to developing the Case-Fisk Alliance and an Envoys program in Nashville.

The first CLiPS faculty hire at Case, which targeted members of underrepresented minorities, was hired. Dr. LaShanda Korley joined the faculty of the Department of Macromolecular Science on July 1, 2007. A search to fill the second CLiPS faculty position has been initiated. The Case Provost has committed startup funds for the new hire and laboratory space is promised in the Kent Hale Smith Building.

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. Often, platform meetings are combined in order to facilitate interactions and coordination between 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. Four 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. Five 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 provisionary patents or is cleared for external presentation.

As part of the research and education mission, the CLiPS Characterization Laboratories have been established primarily in the Kent Hale Smith Building. In the past year, we expanded our imaging capability with the purchase of an AFM and cryomicrotome. A rotating anode generator and its position sensitive WAXS detector were renovated and equipped with SAXS. A comprehensive laboratory in dielectric characterization was built. Additional investments were made in the laser and optics laboratories, which are located nearby. These additions complement the existing comprehensive laboratories for gas transport, thermal analysis, mechanical testing and biaxial orientation. We anticipate future investments in rheological characterization and in the process laboratory. The instrumental facilities are maintained with the assistance of a laboratory technician.

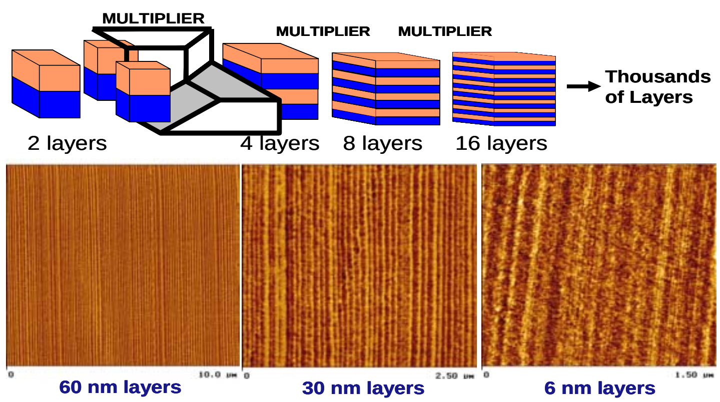
Intellectual Merit of the Center

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 interphase properties 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 security, health, environment, and energy.

To achieve these goals, the research programs are organized into research platforms. This year, the initial three platforms were expanded to four. New opportunities for science and application of the layer-multiplying technology, which were previously part of Platform I, now form Platform IV under the leadership of Anne Hiltner.



Layer Multiplying Coextrusion Technology

- 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 Optic and Electronic Systems are based on advanced layered materials. Teams from Case, Fisk, Rose-Hulman, 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.

Platform I – Enabling Technology

Platform I supports a continuous coextrusion process that facilitates creation of microlayered and nanolayered systems by forced assembly of polymers on a size scale as small as molecular dimensions, as shown in the figure. This flexible, solvent-free technology accommodates the diverse needs of research in Platforms II, III, and IV. The process is user-friendly and students at all levels gain hands-on laboratory experience in processing layered systems. During the past year, 4 major processing projects are directed toward towards maintaining and expanding the enabling technology.

(1) Efficient and effective operation of the coextrusion process is a key to the success of the CLiPS research goals. Teams of 3 are staffed with graduate students and research associates to maintain and operate the two coextrusion lines. Fourteen graduate students are fully trained in the operation of the co-extrusion process. The processing teams interact with CLiPS research faculty and students through regular web-based meetings with the partner institutions, and through weekly processing team reviews.

Layer uniformity achieved with our system of multiplying is adequate for most of the proposed applications, and the process can be scaled up to commercial operation. However, some of the proposed applications, particularly in the optic and electronic materials, continue to challenge us to achieve better layer uniformity. We dramatically improved layer uniformity by coextruding a thick sacrificial skin layer onto the assembly in a final step before spreading the melt. This also substantially improved the surface quality. It should be noted that in the event that a specific system with strict requirements on layer uniformity is developed for commercialization, an alternative method of layer multiplication is available. This feedblock method is used by 3M to produce high performance optical films and achieves exquisite layer uniformity with hundreds of layers. However, it does not possess the flexibility of our system.

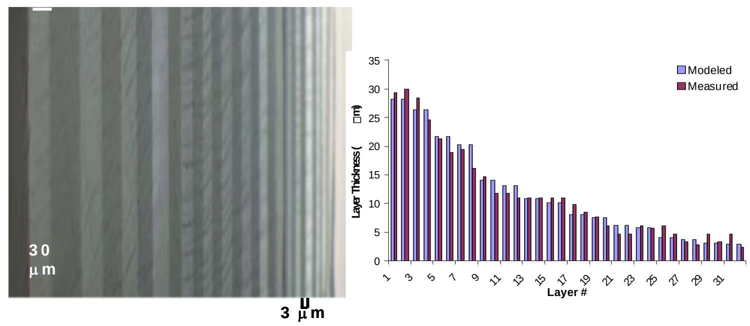
(2) CLiPS researchers indicated a strong need to extend the capabilities of CLiPS enabling microlayering technology to the gram size scale. This would allow the structure-property relationships to be probed for materials previously unavailable for study based on limited availability and high cost. When good layer uniformity could not be achieved with miniaturized multiplying dies due to the frictional edge effects on the polymer melt at the miniaturized multiplier walls, an alternative approach was required. The alternative approach focused on modifying the existing co-extrusion system using recent advances in melt pump technology which are capable of precise flow metering as low as 10 gram/hr. Very low flow rates are achieved by inline inclusion of a special Mini-max injection system. The concept is to precisely inject a small amount of material into one of the alternating layers as the process is running. The system was installed in 2007-08 and co-extrusion trials with gram-scale batches of materials were successful. The injection-modified co-extrusion process is now available for evaluation of its full potential in all areas of CLiPS research.

Students Operating the Coextrusion Process

(3) CLiPS provides the opportunity to extend the boundaries of the current coextrusion system to new and exciting frontiers. Developing multilayer structures with a gradient in the layer thickness distribution could lead to novel optical, transport, and mechanical properties. Offsetting the split position in the current layer multiplication die flow channels would allow the creation of films with two different layer thicknesses.

A gradient in the layer thickness was achieved by replacing the conventional multipliers that evenly split the melt stream with multipliers having an “uneven” split channel. In contrast to the feedblock approach used by 3M Corporation to produce gradient layering, the multiplier approach provides considerable flexibility in the gradient by varying the split ratio and sequencing of the “uneven” multipliers.

For the initial experiments, we designed four multipliers with ‘uneven’ split ratios 50.6/49.4, 51.6/48.4, 53.5/46.5, and 58/42. A 32 layer PS/PMMA film was coextruded with the four “uneven” split layer multipliers aligned from smallest to largest. A microtomed cross-section of the coextruded gradient layer film shows the gradient in layer thickness with a 10X difference between the thickest, 30 µm, and thinnest, 3µm. The figure demonstrates the excellent correspondence between the measured thickness distribution and that calculated from the split ratios. In the coming year, CLiPS researchers will explore the large design space of the gradient layer thickness distributions with analytical models to identify specific gradient layer distributions and producing layered films with novel optical properties.



Cross-section of a 32 layer PS/PMMA gradient layer film produced by ‘uneven’ split layer multiplication (left); and comparison of the measured and calculated layer thickness distribution (right)..

(4) Additional opportunities exist if the layers can be turned around. 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 layer 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.

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 from a variety of polymers. The vertical layers show some undesirable curvature. The origin of the curvature is thought to be differences in the vertically layered melt stream velocity flow profile in the multipliers and exit die.

Future research will focus on eliminating or reducing the vertical layer curvature. Initial studies of the vertically layered films and taps are part of Platform IV and concern the effect of the interphase and layer orientation on anisotropic properties of the layered films.

<u>Platform II – Membranes and Transport Phenomena</u>

Platform II focuses on mass transport phenomena and, more specifically, on membranes and barrier materials. Eight multi-investigator research teams were created, and seven of them 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. This understanding of fundamental transport phenomena will be used to design and optimize unique layered systems for food and electronic packaging, drug delivery and diagnostic devices. Layered material systems will be optimized to exhibit transport-property profiles that may be otherwise inaccessible.

(1) The research on oxygen scavengers for packaging applications has been initiated using polybutadiene. Initial efforts to build a foundation in modeling the scavenging performance were

undertaken. Currently, this approach is being extended to block copolymers containing polybutadiene, such as the Kraton family of materials from Kraton Polymers. Such materials could be used to provide scavenging centers. For example, a polystyrene layer will be co-extruded in microlayer format with a Kraton to give an additional degree of freedom to tune the scavenging performance of a composite layered film. Oxygen scavenging performance of first-generation stand-alone materials have been accomplished and we are planning initial experiments to understand the influence of layering on oxygen scavenging. Additionally, we have launched a modeling effort to complement the experimental effort under way at UT.

(2) Research on layered materials for controlled atmosphere packaging has begun using the PEBAX family of themoplastic elastomers. Initial efforts have focused on learning to use permeation equipment to make single gas permeation measurements. We are now extending this research to block copolymers containing ethylene oxide (and related, high CO_2/O_2 selectivity materials), such as the PEBAX family of thermoplastic elastomers and related materials that could be synthesized through resources available in the Center. Such materials would be co-extruded with thermal switching materials to provide both highly sensitive control of the overall gas transport rate through the structure and high CO_2/O_2 selectivity.

(3) Studies on enzymatically-active membranes for separation and barrier applications have begun using the PEBAX family of thermoplastic elastomers. Initial efforts have focused on learning to characterize enzyme activity and identifying a good enzyme candidate. In this regard, we have decided to begin with lysozyme, which is available in large quantities. It has good anti-bacterial properties for use as an antibacterial additive to layered structures. It should be emphasized that this focus on both molecular biology and chemical engineering would be initiating a unique interdisciplinary training program that should prove interesting to other students and educators. During this first year of the program, most of the research is being focused on developing the student's ability to prepare, characterize, and immobilize enzymes, and to learn the analytical techniques necessary to monitor both the ingress of enzymes into normal membranes and foamed materials. The student working on this project, Mr. Dan Miller, and an undergraduate mentee working with him, Victor Ho, both won National Science Foundation Graduate Research Fellowship Program Awards in March 2008. As a result, Dan will be continuing the enzyme project under sponsorship of the NSF Graduate Fellowship program, and this project will be sunsetted from CLiPS, which will give us the opportunity to add a new student to the research program during the upcoming year. Victor Ho, after completing a successful undergraduate research project sponsored by CLiPS, will attend the University of California, Berkeley this coming Fall to pursue a Ph.D. in Chemical Engineering.

(4) Layered polymeric films aimed at having structures with controlled CO_2/O_2 selectivity have been prepared. Blends of ethylene-acrylic acid copolymer (EAA) with up to 50% polyethylene oxide (PEO) were prepared and characterized in terms of thermal behavior and gas transport. Initially, it was found that when PEO was dispersed as small domains in the EAA matrix, the PEO particles did not crystallize during cooling to ambient temperature. This occurred because most of the PEO particles did not contain a sufficiently active heterogeneous nucleant. As a consequence, the permeability to both O_2 and CO_2 increased substantially without affecting the high selectivity of PEO for CO_2. During the first year, we also co-extruded the first microlayers of EAA and PEO. The individual layers were relatively thick, and the layers exhibited the properties of the constituents. A series model accurately described the gas transport properties. During this past year, this program was extended to investigations of ultrathin layered systems down to the nano-scale. Surprisingly, in ultrathin layers, the PEO crystallizes to a very significant extent, and barrier properties increase more than one order of magnitude as a result. This is, we believe, the first example of directed crystal formation in layered systems to achieve high barrier properties. This rather serendipitous result will be pursued vigorously in the coming year to better understand the molecular origin of the phenomenon that leads to such startling increases in barrier properties. In any event, this project provides an excellent example of new science emerging from the CLiPS program.

(5) Glasses having low glass transition temperatures have been prepared for polymer/glass layered composites with very high barrier. A family of phosphate glasses with T_g values ranging from 90 – 150°C, and moisture regain values of 0.7 – 4% have been produced. A 117°C T_g glass has been chosen as the first material to be evaluated in combination with polypropylene. Melt mixing the inorganic glass with polypropylene and maleated polypropylene produced a range of materials ranging from nearly transparent to opaque. Under polypropylene processing conditions, the inorganic glass was shown to be stable for over an hour, and no major processing problems are anticipated. Current efforts are focused on finding a rheological match of glass and polymer at a single processing temperature. Initial results show that polypropylene/glass blends exhibit polypropylene-like viscosity behavior, and that neat glass and neat polypropylene rheologies can also be closely matched. Both unoriented and biaxially-oriented films of phosphate glass/polypropylene were produced and characterized. Orientation of glass particles will be studied as a function of glass T_g values and incorporation of maleated polymer coupling agent.

(6) The use of inorganic particulates for high barrier systems is being explored in multilayered composites. Research has begun towards optimizing the amount of LLDPE-g-MA compatibilizer that has to be added to disperse the clay in LLDPE. Improvement of clay dispersion with adding more of LLDPE-g-MA has been achieved. At about 10 wt% LLDPE-g-MA, the corresponding nanocomposite diffractograms became practically featureless suggesting exfoliation of the mineral layers. TEM conducted on these same systems are in agreement with the X-ray observations. Currently these nanocomposite compositions are being optimized to achieve the best mineral layer dispersion. The corresponding nanocomposites and pure polymer systems will then be co-extruded into multilayered systems and predictive models for gas diffusion in these systems will be created.

(7) A project related to the low Tg glass project has been launched at Fisk University during this past year. Two compositions of chalcogenide glass were prepared at Fisk. These glasses were $Ge_5Sb_5Se_{90}$ with a T_g of 70 °C, and $Ge_3Se_{95}Sn_2$ having a T_g of 86 °C. For the next year, researchers at Fisk will optimize the process for carbon coating the ampoules. Removing the glass from the quartz ampoule after melting has proven to be difficult and time-consuming due to ingot adherence to the fused quartz. Chipping the glass from the ampoule results in wasted material and also introduces the risk of contaminating the sample with fused quartz fragments. Carbon coating the ampoule sidewalls has proven to be useful in crystal growth experiments since carbon can act as a scavenger of O_2 and H_2O impurities and serve as a protective buffer between the glass and the quartz. The carbon coating process is accomplished by cracking hydrocarbon molecules to produce an amorphous carbon layer. The deposited carbon film is then heated to sufficiently high temperatures to densify the layer into a glass-like form of lower porosity. Such carbon films have proven to be sufficient for preventing ingot adherence to ampoules in CdZnTe crystal growth, and we anticipate that they will serve a similar function in glass processing.

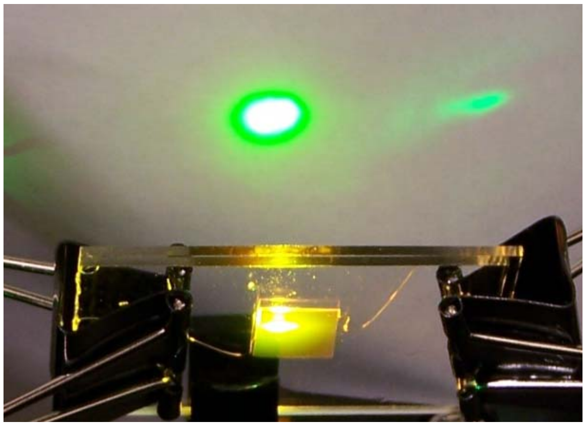
(8) A project in transport modeling in multilayer films was launched at Case this past year. The objectives of this project were to write a generalized computer program to solve the transient one-dimensional diffusion equation in an arbitrary multi-layer membrane, where the number of layers and thickness of each layer is specified, including gradient multilayer films, apply the model to a hypothetic drug delivery device, perform a parametric study to understand the effects of layer spacing/thickness and layer diffusion coefficients on the computed mass delivery (fractional release) profile, analyze and compare transport in gradient multilayer films vs. films with a constant layer spacing, and identify and optimize the multilayer film design (number of layers and spacing between layers) and species diffusion coefficients that will produce a desired mass delivery profile to the external solution in contact with the membrane. However, the PI of this project, Professor Pintauro, is leaving Case to pursue other opportunities. As a result, this project and the modeling needs in Platform II, in general, are being re-evaluated in order to identify the best use of the resources.

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 the last year, two projects, Nonlinear Optics and Optical Limiting were combined into a single project. A new project led by Rose-Hulman in Gradient Refractive Index Optics was initiated. In addition, the project on Photopatterning Films was transferred to Platform I. During this year, each of the four ongoing projects reported major accomplishments, while the new fifth project in gradient index optics also reported significant progress.

(1). A project is underway to investigate Nonlinear Optics and Optical Limiting in multilayered polymer films. The goal is to demonstrate and study nonlinear optical phenomena and devices in active multilayer films utilizing the properties of one-dimensional photonic crystals. Students under the supervision of Profs. Singer, Andrews, Baer, Hiltner, Mu, and Weder are participating in this project. Significant progress in the synthesis and characterization of new nonlinear optical chromophores to be introduced into the multilayering process has taken place. We have synthesized and completed preliminary nonlinear optical measurements of several bis-phenylethynyl-benzene (BPB) and oligo(phenylene vinylene) (cyano-OPV) chromophores having initiated Z-scan measurements of two-photon absorption and nonlinear refractive index. *In a major result, we have identified a nonlinear optical chromophore with an extremely large two-photon cross-section. This crucifore chromophore has a two-photon cross-section of 30,000 GM, which is one of the largest cross-sections reported to date. It is the largest small-molecule value for melt-processible chromophores. A manuscript is in preparation.*

In addition, new facilities for modeling of photonic crystals have been identified and acquired. Crystal Wave finite difference time domain software has been purchased and is being developed. This software can calculate band structures and electromagnetic propagation in active and passive photonic crystals. Other major facilities for pump-probe nonlinear optical measurements have been acquired and are presently being installed. This facility provides for two such setups to be assembled as part of the Center for Chemical Dynamics in the Department of Chemistry. This includes a Spectra-Physics Helios system for transient absorption and reflection in the visible, and a home designed system for infrared studies. These facilities will first be used to characterize the nonlinear optical behavior of multilayer films containing a Pb-phthalocyanine dye, whose linear optical properties have been characterized this year.



(2) Research has been initiated 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 $\mu J/cm^2$ 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. Several publications based on the demonstration, fabrication and physical studies of these lasers are in preparation.

Distributed feedback lasers have been constructed and tested. Laser emission has been observed. Current work proceeds to lower the threshold and increase the efficiency using new polymer materials and improved processing. Physical studies and modeling of laser emission is proceeding.

(3) A unique opportunity to investigate multilayered films in Terahertz Phenomena and Components is in progress. Students under Prof. Shan, Baer, Hiltner, and Weder participate in this project. A THz spectrometer covering the spectral range of 0.1- 1.5 THz in the transmission mode is operational. Homogeneous $BaTiO_3$/polymer nanocomposites have been fabricated using a conventional extrusion techniques. Large enhancement in the RI of the polymer was observed. For instance, in a composite of 18% v/v of $BaTiO_3$/PMMA, an almost 50% increase in the RI was achieved. Further, the FIR or THz properties of the nanocomposites can be predicted by the effective medium theory. *In a major accomplishment, a photonic crystal with a stop band in THz was demonstrated based on $BaTiO_3$/PMMA nanocomposites and PMMA. A publication is under review.*

We have begun to characterize the dielectric response of various polymers in this frequency region. Little research into the dielectric properties of polymers in the terahertz regime has been reported, while doing so could be important for terahertz applications in homeland security. Currently, a THz spectrometer covering frequencies beyond 1-2 THz is being constructed. The new capability will allow us to investigate multilayers of micron layer thicknesses.

(4). Utilization of layered systems in the development of new Electronic Materials and Photovoltaic Effects with photovoltaic properties has shown considerable progress. Students under Profs. Mu, Baer, Hiltner, Singer, Weder participate in this project. In this project, the electronic and photovoltaic properties of ZnO nanostructure-based multifunctional materials are being investigated. In addition, the potential for inorganic-polymeric hybrid and layered solar cells is being explored. Low temperature (~ 500^{o}C) growth of ZnO nanowires on ITO-coated glass substrates is routinely being done in our laboratory. Fabrication of CdTe quantum dots by PED was found to be a very promising approach.

In a major advance, we have demonstrated the photosensitization effect of CdTe quantum dots. Two different device configurations have been investigated. For the first configuration, CdTe is deposited on ZnO before spin coating the P3HT on top. This is followed by thermal treatment and then deposition of zinc electrode. In the second configuration, P3HT is spin coated on ZnO followed by thermal treatment. CdTe is deposited on P3HT and the zinc electrode is deposited on CdTe. Our results show that, in both configurations, the photovoltaic effect of the device is extended to 760 nm. Results were published in Applied Physics Letters.

(5) A new project on Gradient Refractive Index Optics led at Rose-Hulman has been initiated. Profs. Lepkowicz, Bunch, Baer, and Hiltner and their students participate in this project. The primary goal of this research is to identify technology areas in which gradient index optics can have an impact and develop solutions based 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. A laser beam shaping system has been designed in the optical design software package Code V using a single spherical gradient refractive index lens constrained between the indices of refraction of 1.49 to 1.57 and a commercial off the shelf glass lens. Beam shaping plays 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.

In addition, we have designed/optimized, fabricated, and have begun testing a GRIN prism. A GRIN prism differs from a more typical homogenous material prism by creating an optical path difference internally, and demonstrates two key properties: 1) the GRIN prism can be much thinner than homogeneous prisms and 2) the deflection of a GRIN prism is due to an internal index variation and therefore will produce the same deflection angle independent of the surrounding material (i.e. works exactly the same in air as in water). The potential applications for GRIN prisms include beam/image steering, dispersion compensation, and immersed optical systems.

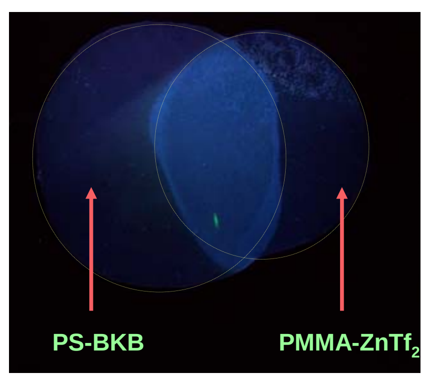
Platform IV – Science and Technology Initiatives

An additional 8 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 and will have to be sunsetted. Indeed, a collaborative project with Fisk on the use of a fluorescent dye to probe the nature of the polymer interphase has been phased out.

(1) Breakup of polymer nanolayers into submicron droplets is a novel approach used by Hiltner and Baer 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^{o}C, which is identified with homogeneous nucleation of the particles in the meso-form. Specific nucleating agents are added to the PP nanolayers in order to study the nature of heterogeneous nucleation of specific polymorphic crystal forms. Initial studies that focused on nucleation of the α-form have been extended to the β-form. This project has already resulted in several publications.

We are also studying crystallization of high density polyethylene (HDPE) droplets obtained in the same way from nanolayers. In collaboration with Galeski and Piorkowska at the Polish Academy of Sciences in Lotz, we are studying the crystallization of HDPE droplets under conditions of high temperature and high pressure where the pseudo-hexagonal phase is formed in HDPE. An important result is that nucleation, presumably heterogeneous, is necessary and advantageous for the formation of the HDPE pseudo-hexagonal phase. A first manuscript has been submitted to Macromolecules.

(2) 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. Work has been done to optimize the purity and scale on which these reactions are done. Both of the macromonomers are now able to be synthesized on a 10-15 gram scale, which will allow for the use of one batch of materials to be used in multiple microlayer experiments. We also established that the macromonomers are thermally stable at the process temperature. Proof of principal was demonstrated by pressing blends of the components into thin films about 30 microns thick. The film of PS contained 1% w/w of the macromonomer and the PMMA film had 1% w/w of zinc triflate. These films were slightly overlapped as seen in the figure and annealed at 190°C for 15 mins. A dramatic change in the fluorescence was seen in the overlap region. This presents strong evidence that self-assembly occurred at the interface. The next step is a coextrusion run utilizing the injection-modified coextrusion process.



Evidence of self-assembly between layers of PS and PMMA containing 1% w/w of macromonomer and zinc triflate, respectively (under UV light)

(3) 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. However, attempts to age the films near the glass transition temperature of PSF resulted in considerable degradation of the EO. The amount of stabilizer in the EO was increased, and the stability at the desired aging temperature increased from 4 to 48 hours. New microlayered films were successfully coextruded. The aging response will be studied at

UT by the gas permeation response of these films as a function of aging time. The first steps of the evaluation by permeation, i.e. to construct gas permeation cells for this project, to eliminate the leaks and to calibrate the cells, have been completed. The gas permeation measurements are supplemented with thermal analysis, which is conventionally used to characterize physical aging of polymers.

(4) Photopatternable films can be produced by incorporating an additive in one of the layers that, on exposure to high intensity UV radiation, will permanently change the refractive index of the photorecctive layers in a controlled fashion. The initial blend system used by Weder and Baer employed cinnamic acid as the photoreactive agent. However, this small molecule diffused and sublimed out of the melt during blending and coextrusion. An alternative approach utilized poly(vinyl cinnamate) (PVCi) which possesses the same reactive chromophores as cinnamic acid.

Alone, PVCi is brittle and undergoes thermal crosslinking at the temperatures required for coextrusion. Blends of PVCi with polystyrene (PS) in 50/50 and 25/75 PS/PVCi compositions showed high refractive index changes of 0.010 – 0.026. Moreover, little or no thermal crosslinking was detected in the blends. A viscosity match was found between the blends and a PMMA resin. This system now awaits microlayering with the injection-modified coextrusion process.

(5) We attempted to combine forced assembly with self-assembly in nanolayers. We successfully coextruded a hydrogenated styrene-b-isoprene copolymer (Kraton® G1730) with polystyrene (Styron 685) as nanolayer films with layer thickness from 7 to 40 nm. However, using oxygen permeability in conjunction with transport models, we did not detect any effect of the confinement on the microphase morphology of the block copolymer. We also found that the self-assembling block copolymers that are commercially available are extremely limited in terms of microphase morphology, composition and rheology.

As a consequence, the project has changed focus, and in the next year, Hiltner, Baer and Korley will concentrate on the effect of confinement on polymer crystallization. The studies of confined crystallization of PEO in Platform II suggest that this will be a timely and fruitful area of investigation. To date, we have fabricated films with micro- and nanolayers of polyamide-6, poly(lactic acid) and polyoxymethylene separated by layers of an amorphous polymer, either polystyrene or polycarbonate. Characterization of these films to obtain the structure and properties of the confined crystalline layer has started.

(6) A new project led by Korley focuses on optimizing the mechanical function of vertical microlayered systems by tuning the adhesive properties of the interphase. The immediate first step is to process straight vertical layers consistently. When processing parameters have been established, a system of materials will be developed that can sustain processing conditions and undergo crosslinking. The processed films will be subjected to UV radiation to invoke crosslinking at the interphase. These interphase-modified materials will then be analyzed to determine the effect of the crosslinking junctions on the mechanical behavior (along and perpendicular to the direct of tensile stretch) of the system. This project is closely interfaced with efforts to convert horizontal layers to vertical layers which are being pursued in Platform I.

Initial efforts involve commercially available materials that are co-extrudable and contain unsaturated groups for crosslinking, such as styrenic block copolymers. Preliminary studies involve solution casting thin films to determine the conditions appropriate for crosslinking of the system. Blends with polyfunctional monomers and photoinitiators are used to examine the thermal stability and degradation of the system.

(7) Two new projects that focus on applications of the coextrusion process in the area of dielectric materials for energy storage are collaborations among Baer and Hiltner at Case, Shirk at the Naval Research Laboratory and Flandin at the University of Savoie. These projects are also aligned with the Case-wide initiatives in energy.

Recent studies have shown that the electrical breakdown strength of polypropylene films depends more on the thickness of the film than on the surface area of the electrode. Decreasing the film thickness results in a substantial increase in breakdown strength, however the effect is not well-understood. Moreover, the limit of the effect for ultra-thin films has not been established. Ultra-thin films with thicknesses on the micron- and submicron-scales are difficult to produce by conventional extrusion methods. We coextrude ultra-thin films of polypropylene between very thick sacrificial skin layers that can be removed after co-extrusion. The sandwiched films can also be biaxially stretched to further reduce the polypropylene film thickness. The first polypropylene films obtained by this method were 1 micron in thickness, but thinner films are possible. Currently, work proceeds on developing a reliable method for measuring the electrical breakdown strength of the ultra-thin films.

(8) The second project in the area of dielectric materials focuses on creating micro- or nanolayered polymer films with high capacitive energy density and low loss by coextruding a high permittivity material and a high breakdown strength material. Considerable effort in the past year was devoted to developing the necessary instrumental capability, and we are now able to reliably characterize the dielectric properties of the films.

An important finding was that the breakdown strength of films that combine a polyvinylidene difluoride-hexafluoropropylene copolymer (high permittivity) with polycarbonate (high breakdown strength) is substantially higher than the additive prediction. The enhanced breakdown strength is attributed to a damage mechanism that is only observed in the layered structures. This 'treeing' phenomenon is now being examined further in order to optimize the material selection and the layered structure design. Preliminary findings also indicate that the layered structures exhibit considerably less hysteresis than monolithic films. This aspect could be extremely important and needs further investigation.

Integration of Research and Education

<u>Vision and Goals</u>

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 will integrate 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 will be 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, create polymer courses for Fisk and Affiliates, and develop advanced modular graduate courses in "polymers plus"
- 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 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. An external evaluator, Dr. Jan Upton, has been engaged to independently evaluate the education initiatives, as well as the diversity efforts.

<u>Course and Curriculum Development</u>

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. CLiPS faculty (Stuart Rowan and others) led the process and worked to ensure that CLiPS-related concepts were included in new courses. The curriculum was completely redesigned in order to:

- Provide fundamental knowledge in polymer science for graduate students who come into the program with a diverse undergraduate background
- Ensure that the curriculum meets the needs of the graduate students from the point of view of their graduate research and their future career development.
- Minimize overlap between courses.
- Offer advanced, interdisciplinary elective courses that include current trends in polymer science and engineering.

Four new "Foundation Courses" were designed which bring all the students, regardless of undergraduate background, 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 (2 credit hour courses) provide the student for 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.

In addition to supporting the revised curriculum, CLiPS at Case sponsors seminars featuring polymer researchers in CLiPS-related areas. In Year 2, CLiPS sponsored three seminars and one full-day symposium featuring five international collaborators. 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. In Year 3, CLiPS will sponsor two seminars for the ACES program (Case NSF ADVANCE) to focus on the impact of female polymer researchers.

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 began a mentoring seminar series in Summer 2007 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 this series was highly positive.

<u>Affiliate Institutions and Education Testbed</u>

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 Affiliates are currently 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 2 a new category was developed called the Education Testbed. This is led by the Plastics Services Network to develop polymer education activities that will be piloted at the Pennsylvania State University at Erie. In consultation with the CLiPS Executive Director for Education, each institution prepares an annual statement of work for CLiPS.

While the continuing institutions often used Year 2 to further activities started in Year 1, the new Affiliate at Youngstown State University has begun some extremely interesting efforts that will expand in coming years. One unique feature that YSU brings to CLiPS is a planetarium. Discussions have begun between Case and YSU on opportunities to use the planetarium to introduce pre-college students and the general public to polymer concepts (i.e. replace constellations with polymer chains). YSU has additionally already initiated course development collaborations with UT and Rose-Hulman. Therefore, this new affiliate relationship with YSU is already showing significant results.

Undergraduate Research

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 2008, the Case SURI program will host two students from Fisk University and six students from CLiPS 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, an annual national conference for undergraduate polymer researchers. ~30 students from 8 universities attended this conference, and prizes were awarded to the top student oral presentations and poster presentations. CLiPS also supports its undergraduate researchers who attend other conferences to present their research.

Pre-College Initiatives

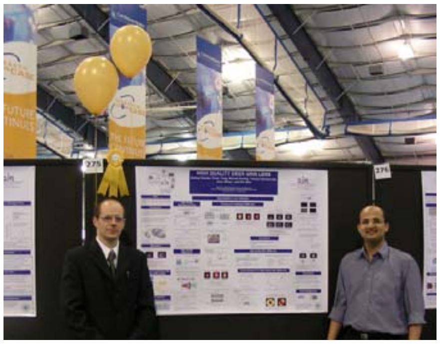
In addition to exposing current college students to polymer science and engineering, CLiPS endeavors to excite and encourage students at a young age to consider such fields. To this end, the Center institutions are developing educational initiatives for pre-college students, especially those in middle school and high school. At Case, relationships have been formed with the Cleveland Metropolitan School District (CMSD) and local private women's high schools, allowing pre-college students to participate in CLiPS research under the supervision of a graduate student and part of a layered research team. The 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 12 students to date, and will have 7 incoming students in Fall 2008. The intent is to translate the model to the CLiPS partners and, after assessment, to the nation. To this end, within CLiPS UT (W07) and RIT (Su07) have also developed PEP sites with their local high schools. UT has sponsored 7 students in their program and RIT has hosted two. Additionally, Fisk is developing a PEP site that will begin in Fall 2008.

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 of the three current seniors have been accepted to Case and plan to matriculate in Fall 2008. 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 is additionally responsible for selecting the high schools involved. In Year 2, the selection process was revised such that schools and teachers involved are those that want to be involved and those that have committed to actively participate in the program. The CMSD works closely with Case to ensure that these efforts stay aligned throughout the duration of the initiatives.

General Education Outreach

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 these formal activities, CLiPS sponsors informal activities that reach out to the community. At The University of Texas, CLiPS sponsors monthly Science Sundays at the Austin Children's Museum. This event engages a large group of pre-college students, as well as their parents.



Case also participates in general outreach activities directed toward the campus and local organizations. On example of a recent event is CLiPS participation in the annual Research ShowCASE in April 2008. CLiPS had a booth at the event that featured a general poster on the Center and examples of the materials produced. Additionally, CLiPS researchers presented posters on their projects, and two 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 goals and objectives for these initiatives as stated below have not changed since the CLiPS Year 1 SIP. However, some deadlines have been modified.

Case-Fisk Alliance

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 collaborative activities will begin in Summer 2008.

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. In Summer 2007, a SURI student from Penn State Erie also spent a week at Fisk to initiate a collaboration between Schiraldi and Morgan involving glasses. 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. The first Fisk alumnus matriculated into a Case PhD program in Fall 2007, two years earlier than planned. This is a major accomplishment and speaks to the positive relationships formed quickly between the two institutions through CLiPS.

Fisk faculty lead and participate in CLiPS research projects. Regular research discussions among Case, Fisk, and the other CLiPS Partner Institutions occur via webconference. These collaborations have produced two co-authored research publications, and numerous single-institution papers on these projects. Faculty, students, and staff at each institution visit the other campus regularly to do research, attend meetings, and present research seminars.

Polymer Envoys Program

The goal of the Polymer Envoys Program is to expose underrepresented students to opportunities in STEM fields at a young age. A summary of the program activities was given in the *Integration of Research and Education* section of this Context Statement. As stated in that section, three programs are currently running: Case/CMSD (Summer 2006), UT/AISD (Winter 2007), and RIT/Rochester East

(Summer 2007). Additionally, Fisk is on track to begin a program in Fall 2008. The UT and Fisk programs will begin at least a year ahead of schedule, while the RIT program was not in the original CLiPS SIP. Owing to the demographics of the pre-college partners, these programs primarily support minority students. Additionally, the programs have been largely female to date.

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 further defined as implementing a high-tech communications infrastructure within the Center that will:

- Facilitate research, education and knowledge transfer within the Center
- Outreach to the community, the nation and the world

The knowledge transfer programs are accomplished through the following:

- Organizing symposia to review Center activities with faculty, students, the CLiPS External Advisory Board and CLiPS industrial investors
- Organizing 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
- Creating and translating courses in polymer science to Fisk University and the Affiliate schools
- Maintaining and updating the CLiPS website on an on-going basis to disseminate information within and beyond the Center
- Facilitating communications across 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 Affiliates Meeting – October 12, 2007. This annual event brings together affiliate faculty from across the Center to formulate work plans for the upcoming year, to generate ideas, and to share strategies.
- CLiPS Investors Meeting – March 12, 2008. 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 23, 2007 and March 13, 2008. A twice yearly meeting to review and advise on the progress of the Center, including areas that need additional focus, and areas where institutional support is needed.
- CLiPS Annual Center Meeting – March 13, 2008. 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 encompassed faculty, staff, and students from all participating institutions, the External Advisory Board, and the CLiPS Investors.

Symposia

Symposia that were designed to communicate information about the Center to a wider audience included:

- INSPIRE Research Conference – September 21-23, 2007. An undergraduate research conference was held in September. The conference attracted thirty students from across the country who participated in workshops and presentations. CLiPS students and faculty members, and the CLiPS program, were highly visible at the conference.

- CLiPS-Sponsored Seminars within the Macromolecular Science & Engineering Seminar Series. October 26, November 9, February 9 - Weekly seminars are a feature of the Department of Macromolecular Science & Engineering at Case. CLiPS sponsors one or two of these seminars per semester engaging speakers whose work is related to that of the Center. The seminars enjoy a large audience and are attended by faculty members and students from across the School of Engineering.

- Advances in Applied Polymer Science Symposium – April 11, 2008. This year's ACS National Meeting and the related ACS Award in Applied Polymer Science Symposium honoring Anne Hiltner gave us the opportunity to invite a number of distinguished international faculty members to visit the Center, to present their research at a day-long symposium titled, "Advanced in Applied Polymer Science," and afterward to engage in face-to-face collaboration with Center faculty members and students. The event provided an opportunity for the Center to continue the celebration of Anne Hiltner's ACS Award in Applied Polymer Science and was well attended by faculty members and students.

- Visit to CLiPS by Case President Barbara Snyder – February 1, 2008. CLiPS' leadership puts forth an on-going effort to inform the university's administration about Center activities. As the in-coming president, this was Barbara Snyder's first visit to CLiPS. She carried on a lively discussion with faculty members, interacted with students, and viewed the processing facility in operation.

Industrial Showcase

An important new symposium that will be realized in the fall of 2008 is the Industrial Showcase. Industrial companies that represent a logical fit for current or potential CLiPS research will be invited to this event. The meeting is envisioned as an opportunity to test the applicability of current CLiPS research projects, to attract industrial partners as potential investors and/or collaborators, and to accelerate the process of developing intellectual property, spinning off projects to industry, and creating new businesses.

To facilitate the Industrial Showcase and related activities, the Center hired a consultant with a background in industry and experience with intellectual property development. Dr. Charles Bush began a part-time position with the Center in February, 2008. Dr. Bush comes from a 32-year career in management of industrial R&D, quality and engineering. He has been involved in the activities of the Department of Macromolecular Science at CWRU and in Professor Baer's and Professor Hiltner's programs in particular for many years. His initial work will be primarily on intellectual property development and on relations with industrial sponsors.

Research and Academic Productivity

The Center's research and academic productivity as evidenced by peer-reviewed publications and presentations has enjoyed dynamic growth over the past year. Center faculty members and students published twenty-three papers in peer reviewed journals, one book chapter, and four additional papers in non-peer reviewed journals. Many of these publications represent the collaborative effort of researchers from across the Center. In addition, Center faculty members gave thirty-one research presentations, Center staff members gave four educational presentations, and students and post-doctoral associates accounted for an additional thirty-three research presentations.

Translation of Education and Diversity Initiatives

Assessments of CLiPS education and diversity initiatives were continued this year. The goal of these assessments is to facilitate the translation of education and diversity programs across sites, as well as the translation of these programs outside of the Center. Key programs being evaluated are the courses and curriculum development initiatives, the Polymer Envoys Program, and the Case-Fisk Alliance. To date these programs have been translated within the Center and to other departments/centers at CLiPS Institutions. In order to more broadly translate these programs, human subjects research approval has been obtained at institutions involved in the assessments. Abstracts and papers on the preliminary results of these assessments were developed in Year 2, and presented at American Chemical Society and

American Society for Engineering Education meetings. These efforts are discussed further in the education section. As necessary, the external evaluator assists in the assessment process.

CLiPS Web Site

The CLiPS web site was published last year and since that time has received over one thousand visitors representing students, educational institutions and industries from around the world. As the Center evolves the web site will be updated on an on-going basis.

Facilitation of Communication across the Center

The more traditional methods of distance communication are used extensively in the day-to-day communication within CLiPS. Meetings of the Executive Committee continue to benefit from teleconferencing. The flexibility of web-based meetings continues to facilitate inclusion of faculty and students at the partner institutions in Platform meetings.

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. To exploit microlayering and nanolayering for commercial applications, important fundamental issues will be addressed in Platform I. Novel and technologically relevant applications, such as membranes and optic/electronic systems, are addressed in Platforms II and III. The fundamental problems and applications are extremely complex, and require 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