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January 6, 2009

CRITICAL NATIONAL NEED IDEA

A 21st Century approach to polymer production, and its impact on energy, environment, and jobs

A White Paper for NIST TIP

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Following discussion with Thomas Wiggins of NIST

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The magnitude of the field

The US chemical industry is on the order of $600 Billion per year, of which roughly 25% is based on the production of polymers and associated chemicals.[*] Polymers are used in vastly different fields, including resins, paints, adhesives, pharmaceuticals, natural biopolymeric products, food and agricultural products, water treatment, oil recovery, paper making, medical devices and supplies, metallurgy, inks and dyes, electronic and optical components, fire resistant materials, roofing and insulating materials, automotive and aeronautical parts, etc. Thus, the value added to the raw polymeric materials themselves is immense.

There are an estimated 13,000 polymer and associated chemical manufacturing sites in the US, that employ at least 570,000 people (2007 census),[†] with production amounting to many billions of pounds per year. The US Chemical industry is the second largest consumer of energy, by industry. Energy use associated with the production portion of the industry was estimated at $7x10^{11}$ kWH (DoE, 1998)[‡]. The polymer industry is one of the major consumers of petroleum and other non-renewable resources. At the same time, estimated employment in the sector fell from 883,000 jobs in 1998 to 576,000 in 2007. Many of these jobs and many abandoned plants have left the US for Asia and other foreign locales in recent years. Reasons for the abandonment include failure of US plants to comply with environmental regulations, insufficient profit margins due to inefficient production processes, and the lure of cheaper labor overseas. This trend continues.

The concept of this White Paper

The concept presented here concerns a paradigm shift in how new polymeric materials are developed and produced at the industrial level, and will carry wide-ranging transformational results economically, industrially, scientifically, and in quality of life. The key technology to be developed is online monitoring and control of polymerization reactions based on fundamental physical and chemical paradigms and constants that are inherently amenable to becoming NIST-compatible criteria for quantitative evaluation and optimization of manufacturing in this sector. The fundamental science component of this will also deepen understanding of polymerization reaction kinetics and mechanisms, leading to accelerated new materials development.

The concept presented here envisions 1) A leap in the novel material properties, quality, versatility, yield, and applications of polymeric materials, 2) the more efficient use of energy, petroleum-based and other non-renewable resources in their manufacture, 3) less greenhouse gas emitted per pound of final product, 4) less chemical contamination of soil, water, air and surrounding communities and 5) enhanced profitability due to the efficiency and quality gains leading to 6) the retention and expansion of an important manufacturing sector in the US, together with the broad spectrum of blue and white collar jobs its provides. 7) A fundamental and quantitative basis for evaluating the efficiency of manufacturing in this sector.

In view of the critical national need for saving our manufacturing industries, innovating to achieve qualitatively and quantitatively new levels of productivity, and addressing growing

[*] http://www.bls.gov/oco/cg/cgs008.htm
[†] http://www.census.gov/epcd/ec97/industry/E325.HTM
[‡] http://www.eia.doe.gov/emeu/mecs/iab98/chemicals/fuel.html

environmental concerns, this vision can be a model for continuous improvement in this field of vital importance.

When one begins to study the manufacturing processes of even the largest, most experienced polymer producers it becomes quickly apparent that there is an enormous potential for efficiency gains in the use of energy, non-renewable resources, and plant and personnel time, as well as for significant reduction in lost production , and environmentally damaging byproducts and emissions. Many manufacturers are wedded to decades old polymerization 'recipes' developed in a bygone era, that can produce a useful product, but not by an efficient path. The gains foreseeable in the concepts presented here might be figuratively compared to those gained in going from wasteful and environmentally damaging coal-fired steam-powered vehicles to modern hybrid, low-emission, high efficiency vehicles. In addition to the great room for improvement in the processes themselves, and the corresponding gains in product quality and energy efficiency this entails, there will be much less failed and sub-standard product. It is common throughout the polymer industry to have elaborate schemes for designating different 'grades' of polymer (often according to the level of sub-standard quality resulting from given production lots), for mixing good and bad product to achieve minimum specifications, and for outright write-off and waste disposal of hopelessly failed product lots.

The means to the vision in this white paper is the development of sophisticated online monitoring and control methods for polymerization development and industrial scale production based on fundamental chemical and physical principles. Whereas the introduction of integrated sensor platforms for small molecule production has been fairly successful in boosting efficiency in the small molecule industry, because the sensors are often very simple, such as temperature, pressure, oxygen, and viscosity, the polymer industry lags far behind due to the intrinsically complex nature of polymers, which are giant molecules with many unusual characteristics. Hence, a central goal of this vision is to develop an arsenal of sophisticated, real time and near real time detection schemes, integrated to fully enabled feedback control systems, that can monitor all the important characteristics embodied in polymerization reactions; reaction kinetics, the rates at which different reagents are consumed, tracing of residual quantities of dangerous reagents, determination of chemical composition distributions, the evolution of molecular weights of polymers, and their architectures and functionality. These latter features to be monitored include branching, grafting, cross-linking, distribution of electrical charge, and the ability of the polymers to undergo phase transitions, form nanostructures and other self-organizing assemblies, and sense and react to environmental factors, such as temperature, light, solvent polarity, specific chemical agents, etc. Furthermore, these detectors and associated feedback controllers should be targeted to work for all, or at least the majority of industrial type polymerization processes: homogeneous and bulk phases, heterogeneous phases such as emulsions, micelles, miniemulsions, and suspensions, slurries, fluidized beds, and for as many mechanisms as possible, such as condensation reactions, free radical polymerization, living type polymerization, including anionic and cationic routes, ring opening metathesis polymerization, and the controlled radical routes such as ATRP (atom transfer radical polymerization, NMP (nitroxide mediated polymerization), and RAFT (reversible addition fragmentation chain transfer).

While the advantages of online polymerization monitoring and control are clear, there is significant risk in the endeavor, where a generalized base of sophisticated principles, instrumentation and approaches needs to be developed and transferred to the demanding reality of the industrial production environment.

The cost of lost opportunity in this area.

Failure to act and innovate in this area means continued closing of US production sites, abandoned towns and devastated economies, continued environmental litigation and diversion of scarce resources into regulatory battles, building the best and most modern facilities overseas, continued wasteful use of non-renewable resources, environmental problems due to greenhouse gases, chemical contamination of soil, water, and air, waste disposal for large tonnages of failed material, and other problems. Regulatory agencies continue to impose stricter standards on chemical products in general, and the failure to comply can lead to further plant shutdowns. Furthermore, increasingly stringent regulations in export markets, such as Europe and Asia, also require increasingly strict adherence to standards and failure in this area will reduce US exports.

Identification of the problems, unmet challenges, and current obstacles

The need to conserve energy, to reduce emissions, and to mitigate soil, air, and water contamination, while creating innovative products, stanching the flow of manufacturing jobs abroad and building new job sectors in the US is massively documented throughout government, trade, and technical publication; e.g. The Bureau of Labor Statistics reports (http://www.bls.gov/oco/cg/cgs008.htm)

> "Another trend in the chemical industry is the rising demand for specialty chemicals. Chemical companies are finding that, in order to remain competitive, they must differentiate their products and produce specialty chemicals, such as advanced polymers and plastics designed for customer-specific uses—for example, a durable body panel on an automobile."

The need for quantitative approaches to polymer characterization has also been highlighted in a detailed survey of leading European polymer industries which established the following high priority targets for maintaining excellence in polymeric materials:[§] (1) better data on reaction kinetics, (2) further development of analytical and quantitative methods of characterizing structure and performance of polymeric materials, and (3) advanced computational techniques to relate polymer properties to molecular structure.

In the polymer industry, one can survey the need for vast innovation of this sort by interviewing polymer plant managers, their upper management, and by reading the polymer reaction engineering and related journals. In these latter, a well developed edifice of theory, computer simulations, and empirical models has been developed for controlling polymerization reactions, in principle, but the weak link continues to be adequate sensors and methods for employing sensors. There has been continued improvement of spectroscopic methods such as *in situ* near infra-red, Fourier transform infra-red, and Raman scattering probes that can be inserted into reactors, but these are often plagued by problems of sensor fouling and dependency upon changing empirical models for data interpretation. There has also been development in the area of comprehensive, absolute approaches to reaction monitoring, such as ACOMP (automatic continuous online monitoring of polymerization reactions) which solves many of the problems of *in situ* sensors through a continuous reactor extraction, dilution and conditioning strategy.[**]

[§] Wegner, G. *European White Book on Fundamental Research in Materials Science*, **2001**, 51-54.

[**] Alina M. Alb, Wayne F. Reed, "Recent advances in ACOMP", Macromolecular Symposia, 271(Modelling, Monitoring and Control of Polymer Properties), 15-25, 2008

No matter how it is approached, there is no single solution for the vast array of different polymers, processes, reactors, and conditions. An entire arsenal of strategies is required that can be used, modularly, to develop and deploy particular solutions effectively for each polymerization production scenario. The development of this arsenal, atop a base of fundamental science, is one of the main goals of this concept.

Industries are tremendously interested in this. The larger industries, such as BASF, DuPont, and Dow, devote considerable resources to finding online monitoring and control solutions to their particular products, whereas smaller producers usually have no resources at all in this area. A central proposition of this concept paper is that if polymer industries are given a chance to participate in a government assisted program with an overarching technological goal of polymerization reaction monitoring and control, they will respond enthusiastically and put up considerable resources of their own in making the endeavor a success.

But the main obstacle currently is that no single company will fund this kind of work in its fundamental and general dimensions, with all the associated risks, since each company is parochially focused on its own product line. Yet, there are so many different types of reactions and schemes involved in the far flung industry that a unified base must be constructed that has an arsenal of adaptive approaches at its disposal. *Hence, current efforts to address the issue of sophisticated, online monitoring and control of polymerization reactions are fragmented into many disjointed efforts, each conceived to address only a very specific problem and reaction/processing scenario.*

Thus, the vision articulated here addresses a range of materials and processes too diverse for support by individual industries. A proposed strategy to overcome this is to form a consortium of interested industries interfacing with a university center(s) of excellence where government action and matching funding provides support for the underlying science and risks and the ‘glue’ to integrate the approach to modular platforms, quickly adaptable to each particular process scenario. Currently, government funding in this area, such as NSF, is too limited in magnitude to allow a project of any girth to be developed. Also, since the intent of the proposed program is to have very short term success and transfer to industry, with resounding societal impact, it may be considered not ‘fundamental enough’ by NSF, despite the project being grounded in fundamental science and engineering.

The technologies to be developed

The technologies to be developed are complete, feedback based systems for real time control and optimization of polymerization reactions in all their vastly different forms. Leading candidates for this include those that make absolute, model-dependent measurements on polymer reaction characteristics in realtime or near-realtime. Such measurements will typically be linked to fundamental physico-chemical phenomena that are well understood, such as light scattering, absorption and emission spectroscopy in different parts of the electromagnetic spectrum (e.g. ultraviolet and infra-red), intrinsic molecular viscosity, quantum spin-based detection such as electron spin resonance and nuclear magnetic resonance, etc. While this strategy does not exclude approaches based on empirical models and calibration schemes, its main virtue is that it provides a hard, physical science foundation for the whole field, yielding reaction measurements (molecular weights, conversion, etc.) among many different types of processes that have a common cross-correlatable and verifiable origin.

This approach, hence, is in keeping with the NIST mission of establishing standards, procedures, and technologies, which are traceable to unambiguous physical and chemical constants and paradigms. With this vision it will be possible in the near future to evaluate polymer manufacturing performance using well defined, NIST-based criteria. This will serve as a benchmark, among other things, for evaluating efficiency and environmental soundness of manufacturing operations.

ACOMP is one of the leading candidates in this area, and achieves the goal of making fundamental measurements by automatically extracting a small stream from the reactor and performing diluting and conditioning steps allowing a train of detectors, such as light scattering, spectrophotometers, and other detectors to characterize absolutely the state of the reaction at each instant. This information will then be used for the basis of feedback control, whereby any and all reaction conditions can be automatically adjusted as needed. These include the flow and concentration of reagents such as monomer, catalysts, initiators, inhibitors, branching agents, quenchers, surfactants, solvents etc., and conditions such as temperature and pressure. The technology is to be used not only in the broadest possible categories of polymerization reaction mechanisms, but also for any given reactor design; batch, semi-continuous, continuous, pressurized, etc. A guiding principle is that the technology used will always be adapted to the chemistry and chemical engineering involved in the reactions and processes, and these latter will never be altered to adapt to the monitoring.

Of course, ACOMP is used only as an example of a new technology that is potentially 'NIST-compatible'. Any other candidate technologies that can adhere to the goal of monitoring the chemical and physical properties of polymerization reactions based on fundamental principles, rather than empirical or inferential schemes, can be considered for development.

Expected outcomes and capabilities.

Pursuing this concept area will yield results outlined above: 1) A leap in the novel material properties, quality, versatility, and applications of polymeric materials, 2) more efficient use of energy, petroleum-based and other non-renewable resources in their manufacture, 3) less greenhouse gas emitted per pound of final product, for all levels of polymers, including commodities, engineering plastics, specialty products, etc. 4) less chemical contamination of soil, water, air and surrounding communities and 5) enhanced profitability due to the efficiency and quality gains 6) the retention and expansion of an important manufacturing sector in the US, together with the broad spectrum of blue and white collar jobs its provides, and 7) the establishment of NIST-compatible metrics for quantitatively evaluating and optimizing manufacturing efficiency in the polymer sector.

Additionally, the use of the technologies developed within academic and industrial Research and Development environments will accelerate the pace of discovery and development of highly specialized and 'intelligent' new polymeric materials. This new generation of polymeric materials will be used for drug and vaccine delivery agents, nanodevices, new medical materials, advanced sensors, self-healing materials, and high performance coatings, optical and electronic materials.

It is expected that, although the program will begin with a small nucleus of polymer producers of various sizes, the efficiency gains and resulting profitability will make it economically imperative that the rest of the polymer industry follow. Thus, the effect will be catalytic, and those industries that are unwilling to modernize to become more energy efficient and environmentally positive will simply become economically uncompetitive. This is why this vision is ultimately a transformational one, in which a whole new manufacturing paradigm across the broad polymer industry results.

The more quickly this technology can be made available, the better. One reason is that construction of polymerization reactors is a very costly undertaking, and the new generation of reactors should have the proposed monitoring and control technology built in as an integral part. As for existing plants, the challenge will be back integration of the new technology into them.

Path to achieving these goals and relation to critical national need selection criteria.

The concept for achieving these goals involves a truly dynamic Government-University-Industry collaboration. As mentioned, industries are already extremely interested in online monitoring and control of polymerization reactions and are devoting resources to it, each in their own way, without any tangible unifying programs and without taking any considerable risks. The government portion addresses the risks involved with developing a fundamental and comprehensive polymerization reaction and control platform.

The suggested model for the vision presented here is that University center(s) of excellence will act as the nexus for the Government-Industry interface. The University will assemble a nucleus or consortium of participating industries who participate in this plan's vision. These industries will be of two types; the first are the polymer producers themselves, and the second are the industries that will produce the online monitoring and control technology, which are usually instrumentation and automation companies, not chemical companies.

These industries will invest in all the aspects required to transfer the developing technology to their own operations, without compromising the confidentiality or their own products and processes, and will also contribute a percentage to the University based R&D work. The Government will fund that part of the University based R&D that is too fundamental, risky, and general for individual companies to invest in; e.g. The University may develop online monitoring and control strategies for polymers that are still in the experimental stage and far from industrial production, or it may invest in major new capabilities (e.g. online electron spin resonance) that no company will fund by itself. In this way, the Government provides the means of growing the technology into a transformational capability for industry and society, while Industry bears the cost of specific embodiments and implementation in their own sector for their own benefit. Furthermore, a government agency such as NIST can use its own intellectual resources, in conjunction with Industry and University, to establish new levels and criteria for quantitatively assessing the polymer manufacturing enterprise. This type of unified, collaborative Government-University-Industry approach will be much more efficient than the scattered, disjoint efforts currently taking place, and the costs will be reduced by avoiding the expense of several competing efforts.

An example of a University center of excellence that could be seen as a paradigm of this model is the Tulane Center for Polymer Reaction Monitoring and Characterization (PolyRMC). This center has invented and pioneered ACOMP development both for R&D in polymer science and engineering, and to aid industries in process optimization, so far only at the bench level. *PolyRMC already has a broad base of participating industries, so that the type of R&D proposed here will go forward whether the Government participates or not. The effect of the Government supporting such work, however, could be profound, and vastly accelerate widespread industrial implementation with all the beneficial consequences proposed in this vision.*

Clearly, Government support in this area would be a winning proposition all ways around: Industries will enlarge their involvement in this area knowing that it corresponds to National priorities and has Government support for the fundamental and high-risk areas of the endeavor. The University, besides having its educational and research mission enhanced, will achieve a goal much more rarely attained; playing a seminal role in developing technology immediately relevant to the real world and providing a well defined mechanism for transfer to industry. The Society hence wins in improving quality of life through better products, more environmentally positive manufacturing, and the prospect of good jobs in an efficient industrial paradigm. The Government wins in that its mission to enhance both fundamental science and rapidly provide benefits to the larger Society are fulfilled, while specific agencies, such as NIST, can fulfill part of their mission by establishing the new technology on a fundamental and quantifiable basis.