The Role of Polymer Research in Green Chemistry and Engineering

Workshop Report

Hosts:

University of Massachusetts
Amherst, Massachusetts
June 11-12, 1998

National Environmental Technology for Waste Prevention Institute (NETI)
Center for Umass/Industry Research on Polymers (CUMIRP)

Sponsors:

U.S. Department of Energy
U.S. Environmental Protection Agency

Prepared by
Energetics, Incorporated
Columbia, Maryland

Overview

Alternative processing describes techniques that are more environmentally benign than those currently in use. Alternative processing can be used to achieve more efficient use of resources (e.g., energy, raw materials) and reduce impacts on human health and safety. The benefits of applying alternative processes go far beyond improving the environment. Replacement of current processes with more benign alternatives can impact the use of precious resources as well as the economic viability of U.S. industry. Using alternatives in chemical reactions has the potential to increase yields, replace toxic and hazardous media, reduce energy consumption and waste generation, and lower production costs. Alternative processes could also be used to achieve improvements in quality control and allow for safer equipment and process design.

The National Environmental Technology for Waste Prevention Institute (NETI) and the Center for UMass/Industry Research on Polymers (CUMIRP) at the University of Massachusetts Amherst hosted a workshop in June 1998 to explore the potential for alternative polymer processes. The Green Chemistry Institute and the Environmental Protection Agency sponsored the workshop; the U.S. Department of Energy and Environmental Protection Agency assisted with planning and facilitation. The workshop was attended by participants from industry, government, academia, and national laboratories (a participant list is provided in Appendix A).

The focus of the workshop was on three major areas of application:

- *Modeling and Simulation of New Polymers and Processes*
- *Synthesis and Catalysis for Environmentally Benign Polymers*
- *Benign Processing and Alternative Reaction Media*

Within each of these areas, participants discussed industry opportunities, performance targets for the future, key technology barriers, and priority research needs.

Participants were asked to look ahead as far as 2020, and to generate “out-of-the-box” ideas that could potentially be achieved within this time frame. The intent was to develop a research agenda in keeping with *Technology Vision 2020: The U.S. Chemical Industry* (available from the American Chemical Society, Washington, D.C. 202-452-8917). *Technology Vision 2020*, developed by technical and business leaders in the chemical industry, describes a vision for the industry over the next 25 years. It also outlines the competitive and societal challenges the industry will face, and the technical areas where advances will be critical if the industry is to achieve its vision.

This report summarizes the results of the workshop, and provides detailed tables for industry opportunities, goals, barriers and research needs.

Industry Opportunities for Alternative Polymer Processing

No other group of compounds has had as great an impact on our day-to-day living as synthetic polymers. Polymers have many uses, from the foam coffee cup to the life-saving artificial heart valve. Replacement of traditional materials such as metals, wood, glass, and natural fibers with synthetic polymers and composite materials has resulted in products with lower weight, better energy efficiency, higher performance and durability, and increased design and manufacturing flexibility. Polymer synthesis is a major part of the chemical industry with annual production exceeding 30 million tons per year.

Exhibit 1. Industry Opportunities/ Problem Areas
Polymer Modeling

- Focus on commodity polymers--largest volume, largest waste
- Model/design polymer from "cradle to grave"
    - Systems engineering approach
    - Model physical, chemical, toxicological properties of feedstocks, intermediates and degradation products
    - Design manufacturing process at same time as synthesis pathways
    - Predict polymer material properties, including effects of processing
    - Predict and minimize waste fraction and by-products
    - Predict recyclability
- Develop test methods that correlate with molecular-based predictions
- Develop molecular-based predictions that correlate with chemical, structural and mechanical properties
- Develop artificial intelligence or equivalent methods to match polymer with end-use needs
- Design polymer features to minimize/ eliminate additives

Modeling plays an integral part in the process of producing new polymers and synthesis methods. Improved modeling of polymeric processes could result in reduced waste and energy use, as well as reduced start-up times (See Exhibit 1). Potential industry opportunities with respect to polymer modeling include predicting material properties and process effects on properties as well as developing test methods to predict properties. Developing new chemical pathways to and from materials is a great potential use for polymer process models. Models will allow scientists and engineers to design better products and processes with less trial and error on the bench and pilot scales.

New methods for polymer processing and synthesis could reduce or eliminate the environmental problems that are associated with polymer manufacturing as well as increase energy efficiency and decrease waste generation (See Exhibit 2). Utilizing alternative raw materials is one way of improving material utilization and efficiency in the polymer industry. Materials that may be considered waste in one segment of the industry could become raw materials for polymer synthesis. Combining the processes of polymerization and fabrication is another area where novel techniques could decrease processing unit steps and thereby increase productivity and efficiency. Product recycling and recyclability is a potentially large area in which alternative processing and polymer synthesis could have a substantial impact.

Polymer manufacturing has traditionally involved the use of volatile organic solvents and water and has required extensive separation and containment processes to ensure that harmful materials do not enter the environment. Alternative reaction media (see inset) could reduce or replace solvents that are currently in use for polymer synthesis and processing. Examples of a benign process occurring in an alternative reaction media include solvent-free coatings, polymerization reactions that take place within an organism such as a plant or bacterium, and reactions within a dispersed or continuous polymer phase dilated by supercritical fluids (SCF's) such as carbon dioxide.

Potential Alternative Reaction Media

- Melt phase chemistry
- Carbon dioxide as a benign plasticizer for polymer melts and dispersions
- Solid-state chemistry
- Interfacial and colloidal chemistry including:
  - S Liquid - solid
  - S Supercritical fluid - liquid
  - S Supercritical fluid - solid
  - S Vapor - solid
- Low vapor pressure organic liquids
- Low vapor pressure ionic liquids
- Solvent-free coatings
- Biological systems

Benign processing and alternative reaction media has the potential to completely change the methods in which polymers are currently being produced (See Exhibit 3). As environmental standards increase, methods to produce polymers in ways that either decrease the amounts of organic solvents being used or increase their recyclability will become more important.

Exhibit 2. Industry Opportunities/ Problem Areas
Polymer Processing and Synthesis

- Renewable resources, by-products and plastic waste for monomers and polymer production
- Exploit new genetic tools for new biopolymers and monomer production
- New benign catalysts
- Simplification of materials in order to simplify processing and recycling
- Improved synthesis of monomers to utilize by-products and reduce energy requirements
- Increased use of enzymes for monomer synthesis and polymerization reactions
- Application of combinatorial chemistry to the design of new and improved catalysts

Exhibit 3. Industry Opportunities/ Problem Areas
Benign Processing and Alternative Reaction Media

- Solvent emissions
- Energy costs
- Renewable feedstock/domestic feedstock
- Polymer recovery
- "Green" coatings
- Reduction of solid waste/increase in yields
- Meet greenhouse goals/tariff advantages
- Universal recycling processes
- Alternative feedstocks
- Monomer recovery/depolymerization
- Materials efficiency (strength/weight)
- Thermally stable polymers
- Develop new materials without going back to the monomer
- New materials with enhanced properties
- Elimination of finishing steps

Performance Targets for Synthesis and Polymer Processing Technology

The Chemical Industry Vision 2020 lists the following goals for the polymer industry :

- *Scientists will be able to design polymers and predict their properties, from the molecular level through the macroscopic level, relying on easy to use computational tools.*
- *Scientists will be able to manipulate polymers precisely - from nanoscale to macroscale - for economical synthesis, processing, and manufacturing of lower cost, higher performance materials.*
- *There will be increased acceptance of methods for disassembly and reuse, and life-cycle considerations as parts of polymer development.*

The performance targets shown in Exhibits 4 through 6 closely follow the goals stated in the vision. By the year 2020, the polymer industry will have improved its products while decreasing waste and energy use.

Exhibit 4. Overarching Performance Targets
Polymer Modeling

- Increase use of solvent-free processes
- Reduce development time
- Improve design of catalysts
- Create polymer design for processing as well as for use requirements
- Integrate the following into models:
  - Recycling
  - Recyclability
  - Zero waste/zero transitional product
- Apply a life-cycle systems approach to modeling

Specific Performance Targets
Polymer Modeling

- Design of polymers and processes will shift from purely experimental to a modeling/design/experiment approach
- Models that span a range of length and time scale will exist
- Intermediates will be identified (reaction pathways will be known)
- Durability and wearability will be predictable to design for the long-term
- Morphology will be predictable for all carbon, hydrogen, nitrogen, oxygen, and silicon polymers
- Miscibility of polymers will be predictable
- Activity and selectivity will be predictable

Application of Green Chemistry to Synthesis

General target areas for the application of green chemistry to polymer synthesis will require substantial advances in several areas including: 1) in the selection of reaction conditions for both monomer and polymer synthesis (media, catalysts, by-products, energy reaction); 2) in the application of biological reactions to monomer and polymer synthesis (genetic engineering of microorganisms and plants, enzymes to catalyze reactions, greater interdisciplinary approach, improved downstream processing); 3) improved understanding of structure-property-applications relationship (self-assembly systems, modified biopolymers, lower-cost biodegradable polymers with better properties); and 4) recycling of polymers and plastics (ability to reprocess a much broader range of plastics, controlled chemical and biological depolymerization for monomer recovery).

Exhibit 5. Overarching Performance Targets
Polymer Processing/Synthesis

- Improve energy efficiency by 40 to 50% by the year 2020
- Achieve development of carbon dioxide neutral processes by 2020
- Reduce waste in polymerization processes by 30 to 40% by 2020
- Totally convert solvent-based and water-based processes to "green" processes by 2020

Specific Performance Targets
Polymer Processing/Synthesis

- Energy efficiency in existing polymerization systems will be improved through:
  - Stereospecific catalysts
  - Condensation polymerization
  - Biocatalytic polymerization
  - New synthetic routes/monomers
  - Examine/reduce energy intensity of application of material end-use
- Acid catalysis will be replaced (by 50%) with alternative methods (e.g., heterogeneous, resin-based)
- Low corrosion and biodegradable polymeric cleaners will be developed
- Chemical reactions will be managed through multi-phase systems
- Solid/melt polymerization will be used where possible
- Expand use of light-activated processes
- Expand our menu of "design for the environment" (post-recovery) polymers
- Work toward biodegradable polymers with properties better than polyethylene
- All one-time use polymers will be fully biodegradable and produced from renewable sources

Exhibit 6. Overarching Performance Targets
Benign Processing and Alternative Reaction Media

- Elimination of emissions in polymer manufacture and polymer-based processes
- Eliminate 50% of solvent-based processes
- 50% reduction in energy consumption on a per pound basis
- 100% of raw material utilization
- Achieve 6 ∑ performance by 2020
- 50% reduction in plastics that are landfilled

Specific Performance Targets
Benign Processing and Alternative Reaction Media

- 75% of polymers used will be recycled and/or reused
- Achieve "custom" processing with no waste
- Have new "green" reaction media that span a range of solubilities
- 30% of raw materials will be biomass or bio-derived
- 50% reduction of water in polymer processing
- Polymer/carbon dioxide mixtures will be fully understood
- Life cycle analyses will be publicly available
- Reduction in additives

Improved Energy Efficiency and Decreased Energy Consumption

All of the segments of the polymer industry are working toward the goal of improved energy efficiency. One way that energy will be saved is through processes that will require less separation of final product. Creating polymer synthesis methods that produce less by-product is a primary goal. Use of modeling to predict intermediates and reaction pathways will help achieve this goal. Increasing the amount of polymer that can be recycled is another method of increasing energy efficiency. Improving the energy efficiency of current polymerization systems through creating better stereospecific catalysts, biocatalytic reactions, and condensation polymerization reactions is key to achieving the year 2020 performance targets.

Reduce or Eliminate Volatile Organic Solvents in Polymer Processing

All segments of the polymer industry will have to work together to achieve the goal of reducing or eliminating volatile organic solvents in polymer manufacturing. The industry must find new "green" reaction media that span a range of solubilities. Organic solvents have been traditionally used in the synthesis of polymers because their solubilities fall in the range that is appropriate for polymerization reactions to occur. Developing methods for using alternate solvents such as carbon dioxide, water, or ionic liquids will become important to the elimination of organics. These efforts, however, must not produce contaminated aqueous streams. Using models to predict the miscibility of polymers is both a goal and a means to achieving the target of reduced organic solvent use.

Reduction of Waste and Emissions in Polymer Manufacturing

Another goal that relates to all parts of the industry is the reduction of waste and emissions in polymer processing and synthesis. Reduction of waste can be achieved through improvements in recycling and recyclability, and better management of chemical reactions. The specific performance targets that relate to this goal include: reduction of water in polymer processing, increasing the markets for by-products, and increasing the biodegradability of polymers.

Barriers to Achieving Vision Goals in Polymer Processing and Technology

The technology vision that has been described in the previous section cannot be achieved today because of technological and social/political barriers. The barriers for the three segments of the polymer industry are shown in Appendix B, Exhibits B-1 through B-3. The barriers for all three segments fall into five common categories:

- Poor Fundamental Knowledge
- Market/Economic Issues
- Institutional/Educational Issues
- Basic Science/Predictive Capability
- Computing Capability

Poor Fundamental Knowledge

One of the most important technological barriers in this category is that structures, processing, and property relationships of polymers are not fully understood. Polymers can have highly complex molecular structures and inter-molecular relationships. This can make their macroscopic behaviors very difficult to predict. This lack of knowledge prevents scientists from developing better models and processes for specific polymers. Few reaction media for polymerization reactions are considered "green" and environmentally benign.

Market, Economic, Institutional and Education Issues
Although these barriers do not specifically pertain to technology issues, they do prevent achievement of technological goals by preventing effective research from being conducted. A lack of incentives for industry outside of regulatory areas is a primary barrier to the advancement of the vision. There is a lack of national priority, both in the industry and in government, for promoting the need for improvements in the manufacture of polymers.

Environmentally benign "green" manufacturing is currently seen as more expensive than traditional polymer production. A full life-cycle cost analysis of many products and processes is not available to help determine whether new methods of production will actually help save the industry money in the long-term.

Basic Science/Predictive Capability
In many areas of polymer science, theory has not yet been fully developed to describe many phenomena. Polymer relationships on the microscopic scale are not yet fully understood and cannot therefore be modeled with a high degree of accuracy. The mechanisms of polymer self-assembly are also not yet fully understood. This lack of knowledge prevents tailoring processes to best suit a specific type of polymer and also prevents new polymers being developed for custom applications.

Computing Ability
A key barrier to more effective computational modeling of polymer processing and synthesis is the difficulty in getting around the problem of molecular size. There is a trade off between molecule size and model accuracy because the shift in behavior from the microscopic to the macroscopic scales is very difficult to predict. Although modeling has had great successes (homogeneous catalysis, for example), skepticism about model results can prevent the application and benefits of these techniques.

Research Needs in Polymer Processing and Technology

The research that is needed to reach the performance targets for the year 2020 are described in Appendix C, Exhibits C-1 through C-3. The research needs in these tables are further broken down into time frames. The time frames describe when commercially or otherwise viable results from the research can be expected. The research needs for all three segments generally fall into the same five common categories as the barriers:

- Fundamental Knowledge
- Market/Economic Issues
- Institutional/Educational Issues
- Basic Science/Predictive Capability
- Computing Capability

Fundamental Knowledge
The highest priority research in this category is the need for further study of the chemistry of

alternative reaction media (A.R.M). Research into the solubilities of A.R.M. and their behaviors in polymerization reactions are key to creating new processes. The miscibilities of polymers in the A.R.M. must also be further understood.

A better mechanistic understanding of catalysis is also needed for the advancement of the industry. Many polymeric processes rely heavily on effective catalysts for their completion. With industry looking to replace many traditional solvents with alternatives, the behavior of catalysts under different conditions must be analyzed. Modeling with computational chemistry is a promising technique already employed in the industry with success.

Market, Economic, Institutional and Education Issues

One of the simplest, yet seemingly most difficult solutions to the problems that face the polymer industry is to institute an inter-disciplinarian approach to research. Experimental scientists, modelers, and engineers must work together to exchange their knowledge and expertise to improve processes. There needs to be better industry and end-user appreciation of the utility of modeling and how it relates to the development of new technologies. The initiation of a consortium of industry, academia, and government to develop funding and support mechanisms could be key to advancing the industry.

Basic Science/Predictive Capability

The area of basic science and predictive capability is perhaps the area in which the greatest benefit to the industry can be obtained through effective research. One of the highest priority research needs in this category is to find an improved method of life-cycle analysis. Implementing life-cycle analysis into the development of new processes will help reduce some of the trial and error that occurs in pilot and bench scale research.

Other research needs in this category deal with specific technological issues involved in the manufacturing of polymers. New polymer synthesis from natural products and new separation and purification technology will help achieve the goal of lower emissions and less waste. The ability to measure physical and mechanical properties on-line will allow scientists to better understand the mechanisms involved in polymer synthesis. This will also help scientists develop metabolic engineering to control the structures and features of polymers.

Computing Ability and Modeling

Computational modeling needs to be better recognized in the industry as a key part in the development of better processes and products. Predictive models for reaction pathways can allow scientists to improve reaction selectivity and create fewer undesirable by-products and wastes. The development of integrated models at multiple scales will help unveil the mysteries of polymeric phenomena on the atomic, molecular, and bulk scales. At the same time, these predictive tools will be used to identify and create reaction routes to desired polymers with specific properties. Process modeling and design is another aspect that can be useful. For example, modeling of biological systems should aid development of biological and biomimetic routes.

Appendix A: Workshop Participants

SESSION 1. MODELING AND SIMULATION OF NEW POLYMERS AND PROCESS
Anna C. Balazs, University of Pittsburgh
Jeremy M. Boak, Los Alamos National Laboratory
Linda J. Broadbelt, Northwestern University
Richard D. Kelley, U.S. Department of Energy
Sanat Kumar, Pennsylvania State University
Robert Laurence, University of Massachusetts Amherst
Rose A. Ryntz, Ford Motor Company
Isaac Sanchez, University of Texas
Brian Watson, GE Plastics
Phil Westmoreland, University of Massachusetts Amherst*****

SESSION 2. SYNTHESIS AND CATALYSIS FOR ENVIRONMENTALLY BENIGN POLYMERS
Jawed Asrar, Monsanto Company
Brian Benicewicz, Rennsselaer Polytechnic Institute
Pieter J. Dijkstra, University of Twente/The Netherlands
Michael Gonzalez, EPA/National Risk Management Research Laboratory
Steve Goodwin, University of Massachusetts Amherst
Rich Gross, Polytechnic University
David E. Henton, Dow Chemical Company
Nancy B. Jackson, Sandia National Laboratories
David Kaplan, Tufts University
Steve Kelley, National Renewable Energy Laboratory
Robert Lenz, University of Massachusetts Amherst
Michael D. Paster, Monsanto Company
Jacques Penelle, University of Massachusetts Amherst
Lloyd M. Robeson, Air Products and Chemicals, Inc.*****
Joseph Rogers, American Institute of Chemical Engineering/Center for Waste Reduction Technology
Lee Schechtman, Procter& Gamble
Fawzy Sherif, Akzo Nobel Chemicals

*** CHAIR**

SESSION 3. BENIGN PROCESSING AND REACTION MEDIA

Eric Amis, National Institute of Standards and Technology
Eric Beckman, University of Pittsburgh
Richard Bopp, Cargill-Dow Polymers
Chris Bowman, University of Colorado
Peter Condo, 3M Company
Karen A. Connery, Praxair
Jim Hatfield, Union Carbide
Timothy Long, Eastman Chemical
Thomas McCarthy, University of Massachusetts
Luc Moens, National Renewable Energy Laboratory
Robin D. Rogers, University of Alabama
Chuck Ryan, National Center for Manufacturing Sciences
Barbara Smith, Los Alamos National Laboratory
Kyung W. Suh, Dow Chemical Company
James Watkins, University of Masschusetts Amherst*****
Robert A. Weiss, University of Connecticut

OBSERVERS

Paul Anastas, Environmental Protection Agency
Joseph Breen, Green Chemistry Institute
James Capistran, CUMIRP/University of Massachusetts Amherst
John Carberry, DuPont Experimental Station
Joseph Carra, Environmental Protection Agency
John Flynn, MA Office of Technical Assistance
Dennis Hjeresen, Los Alamos National Laboratory
Joseph Larson, NETI/University of Massachusetts Amherst
Amy Manheim, U.S. Department of Energy
Denise Swink, U.S. Department of Energy
Sharon Tracey, NETI/University of Massachusetts Amherst
Steven C. Weiner, Pacific Northwest National Laboratory/Industries of the Future Laboratory Coordinating Council

*** CHAIR**

Appendix B: Barriers

Exhibit B-1. Barriers To Polymer Modeling

(◆ = Most Critical Problem Areas/Barriers)

Computing Ability	Human Institutional Factors	Basic Knowledge/ Science	Lack of Data	Clearer Definition
Getting around molecular size problem - size/accuracy trade off ◆◆◆ S scan length and time scales (micro to macro) Computer Hardware S speed ◆ Lack of development of force fields to allow modeling of certain properties ◆ Ability to model wearability and durability ◆ Development and verification of hybrid modeling methods (w/communication between different methods) Optimization methods/techniques for "many degrees of freedom" problems Lack of method to model recyclability of materials	Attitude towards use and trust of simulations ◆ Common understanding of what modeling is ◆ Ease of usability of models S in-house theoretical development S platform independent ◆ Cost Excellent minds are leaving polymer modeling chemistry (theoretical physics) Missing out on transferring accomplishments from other industries Lack of cross-disciplinary approach Understanding limitations and output of modeling Interface between modeling and marketing departments	Lack of basic science and understanding ◆◆ Need models that take processing history into account ◆◆ Complexity and diversity of reactions S reactants S blends S product ◆ 3-D crystallinity (length scale) Lack of understanding of interactions with additives Measuring chemical and physical characteristics of material in situ Quantum modeling of transition metals Need better understanding of fluid mechanics of mixing, shear fields, wall effects, etc. S reactor flow modeling with CFD Need way to model toxicity Problems in modeling of photo-degradation Need advances in process models for model-based control S mechanisms to respond to changes Quantitative structure - property relations (structure-based)	Lack of good physical property data S kinetic data ◆◆◆ Lack of micro-structure and defect information ◆	Fuzziness of product description What is "green" in 2020

Exhibit B-2. Barriers To Alternative Polymer Processing/Synthesis

(◆ = Most Critical Problem Areas/Barriers)

Institutional/ Educational	Technology Issues/ Existing/Other New Polymerization	Technology-Other Issues/National Polymers	Basic Science/Predictive Capability	Customer Needs Market Demands	Other
Need higher national priority in funding for fundamental knowledge ◆◆◆◆◆◆◆ Risk-Aversion in present chemical industry ◆◆◆ Public awareness issues on "green" polymer issues ◆◆ Lack of integrated education among chemistry/biochemistry/polymers ◆ Lack of funding for modeling enzymatic/genetic approaches ◆ Improved interaction between polymer synthesis and catalysis areas	Higher cost of "green" manufacturing ◆◆◆◆◆◆◆ ◆◆ Time from discovery to commercialization ◆◆ Catalyst--supported catalyst activity problems ◆ Analytical capabilities to support new processes.	Lack of separation processes for bio-mass based processes ◆◆◆ Scale-up issues for genetically designed polymers ◆ Lower cost delivered by bio-mass–not available now Bio-mass technology not developed to commercial feasibility Integrated process needed for complete feed-stock utilization Development of 100% reliable processes	Lack of knowledge of biosynthetic pathways ◆◆◆◆ Computational chemistry need improvements S improved models S computational speed ◆◆◆◆ Fundamental understanding of polymer self-assembly ◆◆ Polymer structure/bio-activity/bio-degradability relationships? ◆◆ Predictive/modeling of enzyme activity for chemical/ polymer reaction S lack of enzyme mimetics ◆ Lack of combinatorial strategies for polymer development ◆ Genetic pathway manipulation to produce polymers-understanding needed Definition of what the fundamental research needs actually are Adaptation of biomemitic concepts to new material synthesis	Definition of key requirements for specific applications Limited need for new materials Genetic pathway manipulation to produce polymers–understanding needed demands	Lack of new/creative ideas

Exhibit B-3. Barriers to Benign Processing and Alternative Reaction Media

(◆ = Most Critical Problem Areas/Barriers)

Physical/ Chemical Properties	Fundamental Knowledge	Marker/ Economic Issues	Engineering & Equipment	Institutional Issues	Education/ Training
Low mobility in low solvent systems S heat/mass transfer ◆◆ Lack of good compatibilization technologies for mixed polymer stream recovery ◆ Incompatible properties of polymer materials ◆ Tradeoffs between low solvent versus low energy Volatility of monomers without solvent Immiscibility of components Thermal instability of most polymers Negatives associated with molecular weight Limited solvent power of CO_2	Few candidates that are "green" reaction media ◆◆◆◆◆◆◆◆◆ Structures processing, property relationships are not fully understood ◆◆◆ Absence of fundamental data ◆ Lack of understanding of current, non green processes ◆ Don't have catalysts to allow CO_2 as feedstock Lack of lists/libraries S polymer processing aides S green A.R.M. Need continuous processes	Lack of incentives outside of regulatory areas for investing resources ◆◆◆◆ Lack of competitive advantage S lack of drivers ◆ LCA lacks numerical impacts High cost of research (mostly development) Cost of retrofitting equipment Lack of developed markets for green products Lack of infrastructures and markets for post consumer polymer recycling Capital cost is too high Lack of consumer acceptance for higher cost, green products	Lack of infrastructure for CO_2 use (and other supercritical fluids), room temperature ionic liquids Inability to fabricate cost-effective high pressure equipment Lack of instrumentation for online processing Lack of high vacuum equipment (cost-effective) Green chemistry/products tend to make processes more difficult Need continuous processes	Lack of definition of "green" or "environmentally benign" ◆ Is CO_2 holding back efforts to look at other benign materials? Lack of management support for research and development S short term profit motive Lack of support for projects that do not meet regulatory needs Lack of a consistent definition of green chemistry Reluctance to change existing processes	Lack of personnel trained with using supercritical CO_2 or other green technologies

Appendix C: Research Needs

Exhibit C-1. Research Needed to Overcome Barriers to Polymer Modeling

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Data	(What Is Green?) Problem Definition Needs For Data	Model Development Needs	Characteri-zation/ Measurement Tool	Institutional Education	Computa-tional Tools and Equipment
NEAR (0-3 Years)	Physical properties and chemical structures for comparison of models	Compile description of current modeling capabilities **F** Define priority green chemistry problems ✪✪ Data on highest use polymers Data on highest emissions and release products Data on highest waste generating products Focus on growth industries Define requirements of models for wearability and durability Define what is recycling/ consequences for polymer properties Define “benign” in terms of parameters for models Define modeling needs for batch processes	Life-cycle cost/benefit models **M** Finer-grained CFD approach to capture properties **M** Models for alternative reaction media and condition **MM** Develop solvent-free processing methods; simulate Models of different release of additives from polymer	Atomic basis sets for metals	Industry/end-user appreciation of utility of modeling ✪✪✪✪**M**	Algorithms for organizing large data sets, “data mining”

Exhibit C-1. Research Needed to Overcome Barriers to Polymer Modeling

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Data	(What Is Green?) Problem Definition Needs For Data	Model Development Needs	Characteri-zation/ Measurement Tool	Institutional Education	Computa-tional Tools and Equipment
NEAR-MID				Accelerated test methods for toxicity and durability		
MID (3-10 Years)	Control samples for characterization data Collect fundamental data on VLE		Develop force fields from electronic structure calculations **F** Handling of complexity and diversity of entire system of reactions **MFF**	Way to track processing history of a material		Methods for “many degrees of freedom problems”
LONG (>10 Years)	Microstructural properties data; defects and fracture property data **FF**		Formulation models for additives (interactions) **MM** Build wear ability and durability models S photo degradation S diffusive release	Methods to measure additional micro-structural properties **M** Ability to measure physical and mechanical properties in-line ✪✪**MM**		

Exhibit C-1. Research Needed to Overcome Barriers to Polymer Modeling

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Data	(What Is Green?) Problem Definition Needs For Data	Model Development Needs	Characteri-zation/ Measurement Tool	Institutional Education	Computa-tional Tools and Equipment
ONGOING (ALL Periods)	Data on reactivity and catalyst performance Data and relationships for interaction with additives **MFF** S colorants S fillers S dyes S flame retardants S molecular structure S features of each Develop benchmarking data **✪F**	Prioritized targets for property data S environmental insults	Predictive models for reaction pathways S degradation pathways S synthesis S include intermediates ✪✪ Develop integrated models at multiple scales ✪✪✪✪ Analytical modeling Value of information models (sensitivity/ uncertainty) **FF** Validation of appropriate ranges of applicability of models (fluid behavior) Predict macro-properties from molecule properties **✪MMMFFF** Need ability to predict microscopic properties from molecular structure Better understanding of rheological behavior and appropriate technology to model performance		Get industry comfortable with approximations Money S commitment to theoretical modeling in industry S commitment to more basic research	Development of hybrid models **MMFFF** Faster processing speeds S parallelization **✪F** New computational tools

Exhibit C-2. Research Needed to Develop Improved/Benign Polymer Processing/Synthesis

(✪ = Top Priority; M = High Priority; F = Medium Priority)

Time Frame	Basic Science	Process Engineering Needs	Catalysis	Applications	Institutional Education	Feed-stock
NEAR (0-3 Years)	Study of natural polymer properties relative to structure F	Develop needs in plant transformation to speed up R&D/production F	Review catalyst use in polymers assess environmental impact solve if necessary ✪MF Database of catalyst utilization in polymerization environmental impact	Immobilized enzymes for polymerization ✪M Polysaccharide new applications evaluation versus synthetic polymers ✪M	Initiation consortium of industry/ academia/ government to fund area ✪✪✪✪✪ MFF Inter-disciplinarian approach (team) to solve bio-polymers need/problems. (funding) ✪✪✪✪MM F S flexible platinums for teams S exchange of people/ sabbaticals	
NEAR - MID	Research on natural polymer modification structure/property ✪MM Reliable characterization with smaller quantity of materials FF	Improve method of life-cycle analysis of new versus existing 0-5 years S life cycle analysis tool ✪✪✪FFM New processes for CO_2 in chemical/polymer synthesis ✪MFF Genetic engineering approaches to avoid out crossing	Combinatorial methods for catalyst development ✪MF	Green-very selective solvents M Replace heavy metals in coatings with natural based biocides (also catalysts?)	Synthetic catalytic chemistry disciplines improved cooperation MMMF	
MID (3-10 Years)	Better understanding of structural requirements for biodegradability ✪MMFFF Controlled phase transition M	New separation purification technology needed for bio-mass ✪✪MMMFF Total utilization of biomass polymers chemicals energy ✪MMMFF Alternative feed stocks for monomers ✪MMFF	Flexibility of natural catalysts to conduct unnatural reactions ✪✪F	Natural polymers for coatings/adhesives surface properties M Expand knowledge of applications for suspension/enulvar polymerization M Design of polymeric based insecticides/ pesticides-lowered environmental impact MF		

Exhibit C-2. Research Needed to Develop Improved/Benign Polymer Processing/Synthesis

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Basic Science	Process Engineering Needs	Catalysis	Applications	Institutional Education	Feed-stock
MID - LONG	Understanding of polymer matrix can be better designed for cell growth and differentiation ✪			Development of stimuli-responsive polymers "smart materials"		
LONG (>10 Years)	Research into light driven polymerization ✪FFFFF Improved toxicity testing/study natural polymers ✪F Use of high throughput screening for the nonrational design of polymers MMF Study human sensitivity (allergy) to bio-derived polymers FM Study host-guest interactions database of structure/property relationships for proteins	Genetically enhanced plants to produce final product – no conversion necessary MMFF Replace heavy metal ions with low Mw, lower toxicity systems in polymeric systems ✪	Catalysts to polymerize lower purity monomers (eliminate separation process) ✪✪✪MMM F Develop catalysts for C1 chemistry ✪✪✪MMF More robust (green) biocatalytic methods for convenience of complex biomass streams Natural catalysts for non-classical applications bio-patterning			
ONGOING (ALL PERIODS)	Metabolic engineering to control structure and features ✪✪✪✪✪✪✪ ✪✪MMMM New polymer synthesis from natural bio-product derived monomers ✪✪MMMF FFFFF	Design criteria for production of bio-based technology products MF	Better mechanistic understanding of enzymatic catalysis for polymer production ✪✪✪✪✪M MF Techniques for measurement of surface properties catalyst/bio-polymers etc. FF Redesign of	Look for natural polymers to solve emerging applications in LC, NLO, photo sensitive etc. ✪ Develop improved/new "green" concepts for additives ✪ Better understanding of market/application property profile needs F Environmental toxins - study impact of polymer	Integration of genetic engineering capabilities with polymer needs 0-20 years ✪MM Initiate funding educational issues M	Prediction of petro-chemical based feedstock availability

Exhibit C-2. Research Needed to Develop Improved/Benign Polymer Processing/Synthesis

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Basic Science	Process Engineering Needs	Catalysis	Applications	Institutional Education	Feed-stock
	Fundamental processes controlling self-assembly ✪**MFF** Search for new bio-polymers in the environment ✪**MF** Study/understand genomics **MM** Computational modeling of natural polymers to predict properties **M** Assembly - disassembly of biological macromolecules **F** Metabolic pathway kinetic modeling		existing enzymes for new polymer applications	additives **F** Natural/synthetic polymer compatibilization		

Exhibit C-3. Research Needs in Benign Processing and Alternative Reaction Media

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Needs Assessments	Process Design/ Development	Material Design	Basic Science/ Chemistry of Reactions	Modeling/ Simulation
NEAR (0-3 Years)	Analysis of EPA ranking criteria for "green" **F** Need sources of emissions categorized by polymer groups	Process monitoring and process control **✪MF** Need to use extruders as reactors **MFF** Need to recover rejected parts S painted/coated parts Use polymers to sequester "undesirable" materials Need a means for rapid process scale-up S pilot-plant accessibility Better classification of waste streams Study effect of solid-state orientation Need to induce nucleation/ crystallization	Develop and improve solvent-free coatings and films **✪✪✪MM** New compatibilization agents **M** Need thermosets that are stable at room temperature and don't require high temperatures for curing Development of multi-component solvent-free coatings Need nano-composites for improved properties Dendritic polymers to reduce viscosity S colorants S processing aids Develop electrically conductive polymers for solventless coating	Need to know properties of polymer mixtures at high temperatures and pressures **✪✪** Need supercritical fluid properties of non-hazardous materials **F** Define solvent properties for polymers and compare to VOC data **F** Need rheological studies for polymers at critical conditions Need classification of reaction media in terms of solubility properties	Need to compile and check data
MID (3-10 Years)		Need low-emission, high-mobility, continuous processing **✪✪✪MFF** S CO_2 and related as an example Processing methods, for bio-based materials **✪MM**	Need reversible plasticizers S that can be thermally or photolitically decomposed	Use combinatorial methods for A.R.M. (or catalysts) "Green" separations **✪MM** Need reactions in the foam state Physical properties of biomass needed Need to identify alternatives to chlorinated solvent	Need a group contribution model for solvents **MMF** Computational modeling process optimization

Exhibit C-3. Research Needs in Benign Processing and Alternative Reaction Media

(✪ = Top Priority; **M** = High Priority; **F** = Medium Priority)

Time Frame	Needs Assessments	Process Design/ Development	Material Design	Basic Science/ Chemistry of Reactions	Modeling/ Simulation
LONG (>10 Years)				Need catalysts for C_1 feed stocks **MM** Learn how to chemically activate CO_2	Computational means to predict properties of polymers **F**
ONGOING (ALL PERIODS)	Develop libraries of polymer processing needs and green (A.R.M.) Alternative Reaction Media **S** toxicity data **S** physical properties Need to measure the cost-benefit relation of “green”	Need programs for developing solvent-less processes ✪✪✪**MMM MMF** Development of processing methods to alter polymer properties ✪✪✪**MFFF** Need to improve recycling processes **F** Differentiated examples of A.R.M. **S** also measure economics		Study of chemistry in A.R.M. ✪✪✪✪✪✪✪✪**MM FFF** Need a complete characterization of A.R.M. ✪**MMF** Research on property relationships ✪**MF** Need better measurement techniques ✪**FFFFFF** Study types of processes that can be used with A.R.M.	