Environment and Sustainability:

1. Green Chemistry and Engineering Enabled by New Concepts in Fluoropolymers?

2. Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

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Class Philosophy

• “Traditional” Polymer Science
  – Commodities (1950s – 1990s)
  – The field of polymer science is maturing…chemistry is maturing

• The Future in Polymer Science
  – How do you do something innovative that creates value and can positively impact people’s lives?
The Future in Polymer Science

• Advanced methods for synthesis and integrated fabrication/manufacturing
• Advanced applications
  – Microelectronics
  – Fuel cells
  – Security
  – Diagnostics
  – Interface with biology
    » Medical devices
    » Macromolecular therapeutics
    » Sensors
    » Prosthetics
• Not business as usual
  – Enabling materials
  – Multidisciplinary, integrative
  – Intellectual property and the value chain
  – Aggressive entrepreneurship
• Environmental stewardship is front and center
Principles of Green Chemistry
Adapted from: Anastas & Warner; Green Chemistry: Theory and Practice

1. Better to prevent waste than to treat or clean-up waste
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product
3. Synthetic methodologies and products should be designed to use and generate substances with little or no toxicity
4. Energy requirements should be minimized
5. Should use renewable feedstocks
6. Bio-persistence should be avoided
7. Accidents, releases and explosions should be mitigated
Some of the Most Important Materials in the World

Fluoropolymers Applications - Resins

Telecomm Wire & Cabling

Low Permeable Automotive Fuel Hose

Semiconductor Manufacture

High Purity Liquid Handling

Chemical Processing Valves, Lined Piping, Tanks

Aerospace Materials Hydraulic tubing Wire & Cabling Flares
Conventional Polymerization of Fluoroolefins

Aqueous Emulsion or Suspension
- Uses water
- Needs surfactants (PFOS / PFOA / “C-8”)
- Ionic end-groups
- Multi-step clean-up

Non-aqueous Grades
- Uses CFCs & alternatives
- Surfactant free
- Stable end-groups
- Electronic grades
“C-8” / PFOA

- Needed for the manufacture of Teflon, “inert” to strongly electrophilic radicals
- Fluorinated tail needed to adsorb to Teflon polymer particles
- Persistent organic pollutant
- Fluoropolymer manufacturers under siege

Scotchgard Scotched

“Following the fabric protector’s slippery trail to a new class of pollutant”

NYTimes May 2001
PERFLUORINATED POLLUTANT PUZZLE

PFOA is found in human blood, but sources of this persistent compound remain elusive.

Chemical & Engineering News August 30, 2004

30 AUGUST 2004
Environmental Working Group
Teflon Trial Will Be Public

As early as tomorrow, the EPA's Administrative Law Court could select a judge to preside over the Agency's litigation against Teflon maker DuPont. In July, the Agency filed a complaint that the Teflon maker illegally hid for some 20 years data about drinking water near its Teflon plant in Parkersburg, WV and that women who worked there passed the Teflon chemical through their blood to their babies. One of those two babies, born with birth defects resembling those in laboratory rats, was featured on ABC's "20/20" last November.

Just last Friday, August 27, by failing to respond to EPA, DuPont passed up its chance to settle this case confidentially. Now, the Teflon maker could face a public trial and a fine of up to $313 million.

Friday April 21, 2006 (Associated Press)
DuPont hit with a $5 billion class-action lawsuit because of PFOA

DuPont's Washington Works, located along the Ohio River west of Parkersburg, W.Va., has used PFOA for more than five decades to make the Teflon polymer.

DUPONT PHOTO
Reductions are Important…
Elimination is our Commitment

“…today we are committing to eliminate the need to make, buy or use PFOA by 2015….We are encouraged and pleased that our progress to date has been so promising. As a result, we will intensify our efforts by doubling our R&D investment”

DuPont Chairman and CEO, Chad Holliday, Feb 5, 2007

This is GenX
Polymerization of Fluoroolefins in CO\textsubscript{2}

Typical Reaction

- 10-50\% solids
- 3-5 hours @ 35 °C (batch)
- Pressures 70-140 bar at 35 °C
- $<M_n> \approx 10^6$ g/mol w/o CTA

Surfactant Free!

Romack, T. J.; DeSimone, J.M. *Macromolecules* 1995

“Synthesis of Fluoropolymers in Supercritical Carbon Dioxide”
DuPont’s Fayetteville Works
Teflon-in-CO₂ Manufacturing Plant

“DuPont Introduces Fluoropolymers Made with Supercritical CO₂ Technology”
March 22, 2002 (www.dupont.com)
Multifunctional Perfluoropolyethers

Perfluoropolyether Synthesis in Carbon Dioxide by Hexafluoropropylene Photooxidation

Microfluidics Applications

- Inkjet printing technology:
- Drug delivery:
- Lab-on-a-Chip:
- *In vitro* Diagnostics:
- Injection nozzles:

Unmet need: Solvent and Chemically Resistant Polymer-based MF Devices

“Curable PFPEs”

Merging Imprint Lithography, Microfluidics and Fuel Cells

Zhou; Dominey; Rolland; Maynor; Pandya; DeSimone *J. Am. Chem. Soc.* 2006, 128, 12963
Nano-Imprint Lithography and Molding Enabled w/ “Cured PFPE”

“...are you still using (block) polymers...?”

140 nm lines 70 nm spacing

70 nm lines 140 nm spacing

140 nm lines 70 nm spacing

Photovoltaics

The Ideal BHJ structure

- All excitons are formed within a diffusion length of the interface
- Electrons and holes have straight pathways to electrodes: No dead ends
- Polymer chains can be aligned in the pores: enhanced mobility

Problems

- "Ideal" BHJ structure not manufacturable using conventional approaches
- Most excitons can not diffuse to an interface
- Dead ends prevent charge carriers from reaching electrodes
- Charge transport not fast enough to reach the electrodes before recombination occurs
Particle Replication in Non-wetting Templates
PRINT™ Particles

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PRINT™ Organic Nanoparticles
(Cationic PEG Hydrogel Particles)

< 10 femtoliter cavities
8 inch Masters: < 200 nm PRINT Particles

Sterically Stabilized PEG Particles

265 ± 10 nm

400 nm height
Super Capacitors and Electrets

The electrode assembly is placed in a conventional oven at 110 °C for 3 hours.

Polymerizable Ionic Liquids

\[
\begin{align*}
\text{H}_2\text{C} &\equiv \text{CH} \\
\text{C} &\equiv \text{N} \\
\text{SO}_3^- \\
\end{align*}
\]
PRINT™ Particles in Life Sciences: Range of Cargo & Functionalization Opportunities

- Peptides, Proteins, Enzymes
- Imaging agents
- Linker Groups
- Oligos, siRNA, plasmid DNA, splice switching oligos
- Antigens or antibodies
- Viruses, killed bacteria
- Organelles
- Therapeutics
PRINT™ Particle Uptake in Human PC3 and HeLa Cells
Molding of Biological Structures
(w/ Jude Samulski)

Master Template
Adenovirus
“Cured PFPE” Mold
Replicate

TEM Tomography
UC-San Francisco
w/ Rich Spontak

Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- Energy
- Coatings
- Catalysis
- Renewable Materials
- Manufacturing science
- Separations and purification
- Toxicity and environmental stewardship of nanomaterials
- Environmental Stress Cracking of Polymeric Materials
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- **Energy**
  - Harvesting
    - PV
    - Electrets
  - Transmission
  - Conversion
    - Fuel cells
  - Storage
    - Batteries
    - Supercapacitors
  - Conservation
  - Artificial photosynthesis

**Record Efficiency for Plastic Solar Cells**
Researchers find a new way to make cheap and flexible photovoltaic cells. Friday, July 13, 2007
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- Coatings
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

• Catalysis

\[ \text{PhNH}_2 + \text{Cl}-\text{C}-\text{Cl} \rightarrow \text{PhNCHO} + \text{HCl} \]

\[ \text{PhNCHO} \xrightarrow{\Delta} \text{PhN}==\text{C}==\text{O} + \text{HCl} \]
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- **Renewable Materials**

From corn to polymers and fibers

- **Harvesting the corn**
- **Getting sugar from the corn**
- **Fermenter: Turning sugar into a monomer**
- **Turning monomers into polymers**
- **Fibers and fabrics are created**

**DuPont Sorona®** is made from naturally occurring starch in the kernels of corn. In the next five years, researchers plan to find ways to use starch from the entire plant.
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- Manufacturing science

*SOLAR-CELL ROLLOUT*

Cheap, flexible solar cells could help avert the world’s impending energy crisis. That’s a big promise. But a handful of startups and established companies are vying to make good on it, by developing printable devices made of plastics and nanomaterials.
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- Separations & Purification
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- Toxicity and environmental stewardship of nanomaterials

“…either you are at the table, or you are on the menu…”

Chemical Industry Representative about the Environmental Working Group
Research Opportunities and *Unmet* Material & Process Needs in Environment and Sustainability

- Environmental Stress Cracking of Polymeric Materials