Final Report - Non-PFOS Photoacid Generators: Environmentally Friendly Candidates for Next Generation Lithography (Task 425.013)

Christopher Ober, Cornell; Reyes Sierra, U Arizona

Photoacid generators (PAGs) are UV photosensitive compounds that quickly release protons and have been extensively used in chemically amplified resists. In particular ionic PAGs based on perfluorooctane sulfonate (PFOS) have been widely used because of their unique exceptional performance properties. However, the use of PFOS-based PAGs has come under regulation, as environmental investigations revealed toxic properties and bioaccumulation problems with PFOS. PFOS-based and related PAGs have the additional performance issues caused by their highly fluorinated nature. It is thus desirable to develop alternative improved performance PAGs which solve environmental issues.

Our research design and synthesis of environmentally friendly PAGs has focused on incorporating very short fluorinated sequences on sulfonic acids. In addition we have begun to add naturally occurring sugar skeletons into its framework. This approach is, however, expected to resolve current issues related to the lithographic performance and environmental impact of that key material. The Ober Group has assessed the performance of new PAGs at 193 nm with a series of selected commercial and experimental resists (dry and immersion). Work in the Sierra Group has focused on 1) identification of chemical functionalities contributing to increased (bio)degradation potential; 2) evaluation of key environmental properties of the novel PAGs; and 3) testing the validity of selected computer models to predict PAG environmental fate.

Non-PFOS Photoacid Generators: Environmentally Friendly Candidates for Next Generation Lithography

(Task Number: 425.013)

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Undergraduate Students:
- Matthew West, , Chemical & Environmental Engineering, UA

Other Researchers:
- Woo Jin Bae, Postdoctoral Fellow, Materials Science and Engineering, Cornell Univ.
- Yi Yi, Postdoctoral Fellow, Materials Science and Engineering, Cornell University

Cost Share (other than core ERC funding):
- Rohm & Haas Support ($20K) Yi Yi

Objectives

- **Develop PFOS free and environmentally friendly photoacid generators (PAGs) with easily degradable, biomolecular structures for chemically amplified resist application**
- **Develop PAGs with superior imaging performance**
- **Evaluate lithographic performance in selected model 193 nm and EUV resists**
- **Evaluate the environmental aspects of new environmentally friendly PAGs**

ESH Metrics and Impact

1. *Reduction in the use or replacement of ESH-problematic materials*

   Complete replacement of perfluorooctanesulfonate (PFOS) structures including metal salts and photoacid generators in photoresist formulations

2. *Reduction in emission of ESH-problematic material to environment*

   Develop new PAGs that can be readily disposed of in ESH friendly manner

3. *Reduction in the use of natural resources (water and energy)*

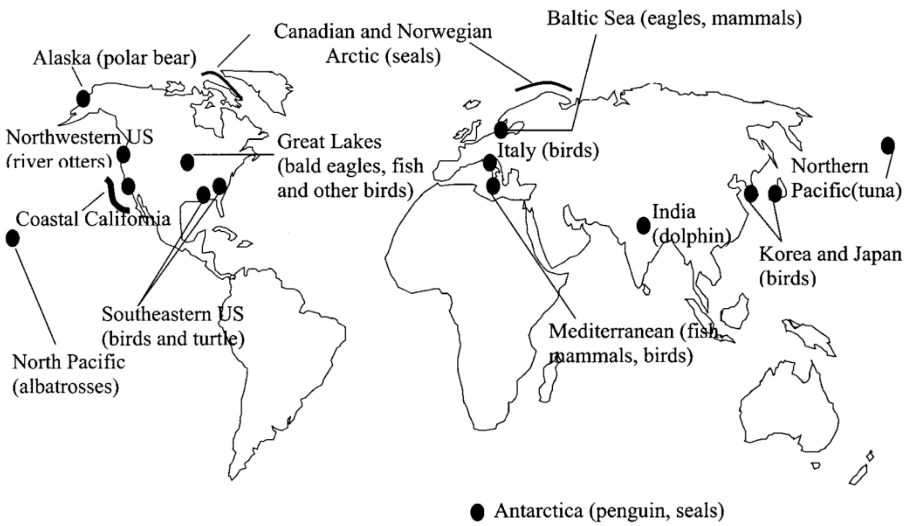
   Prepare new PAGs using simple, energy reduced chemistry in high yields and purity to reduce water use and the use of organic solvents.

4. *Reduction in the use of chemicals*

   By preparing new PAGs using simple chemistry in high yields and purity, we reduce the use of fluorinated chemicals.

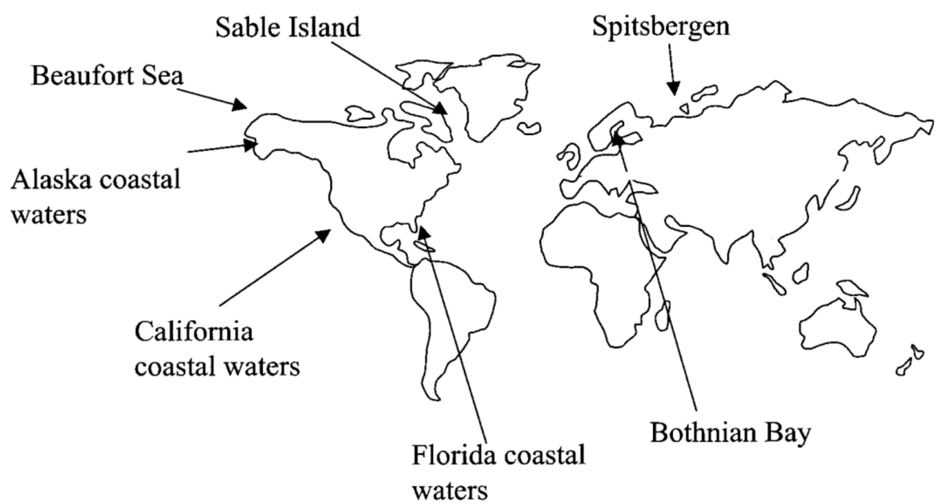
Bioaccumulation of PFOS

Global Distribution of PFOS in Wildlife



***Environ. Sci. Technol.* 2001, *35*, 1339.**

Accumulation of PFOS in Marine Mammals



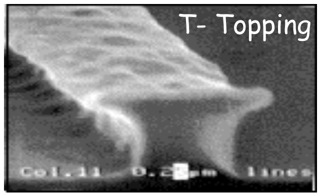
***Environ. Sci. Technol.* 2001, *35*, 1593.**

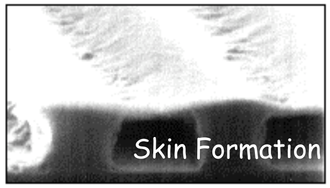
The EPA proposed a significant new use rule (SNUR) for PFOS in 2000.

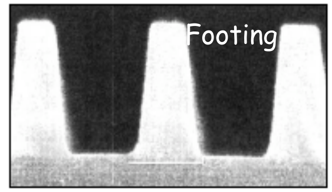
Next Generation PAGs – environmentally friendly, no bioaccumulation

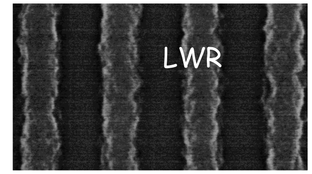
PFOS PAG Performance Issues

"Segregation or non-uniform distribution of PAG"



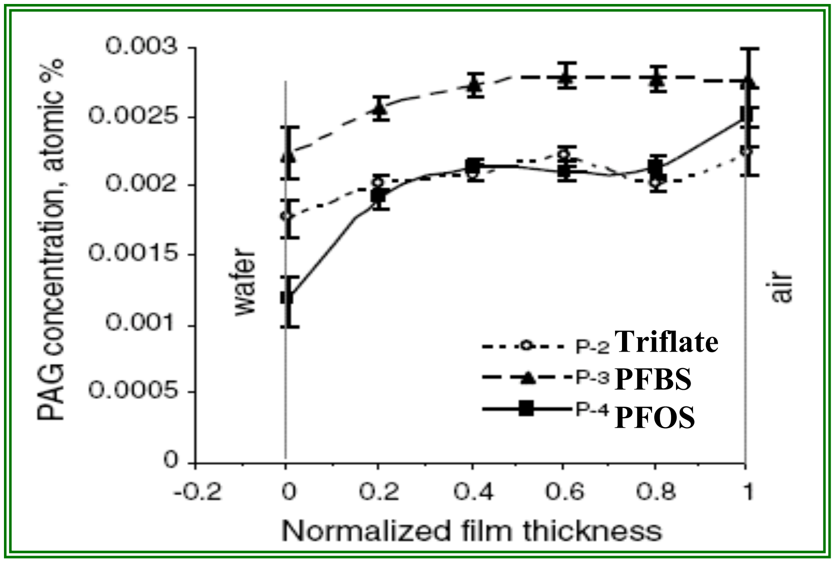




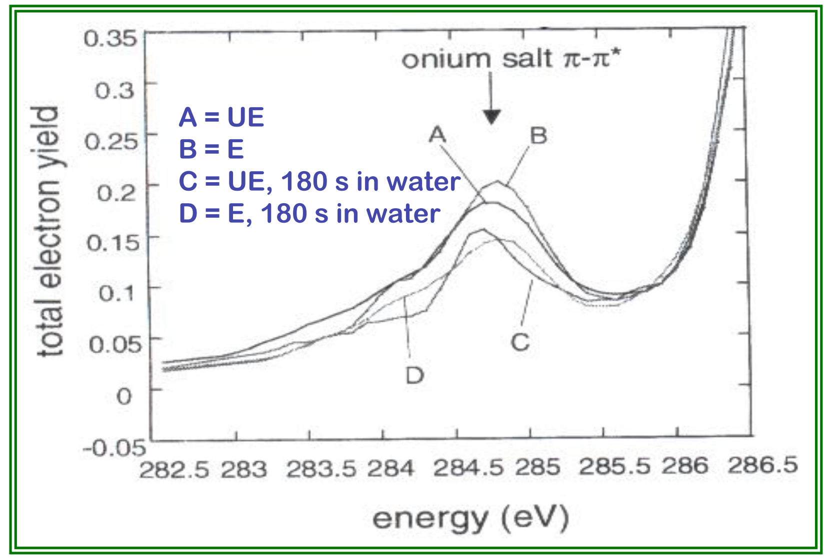


"Surface segregation increases with increase in fluorine content"

"PAG leaching Surface Phenomena"



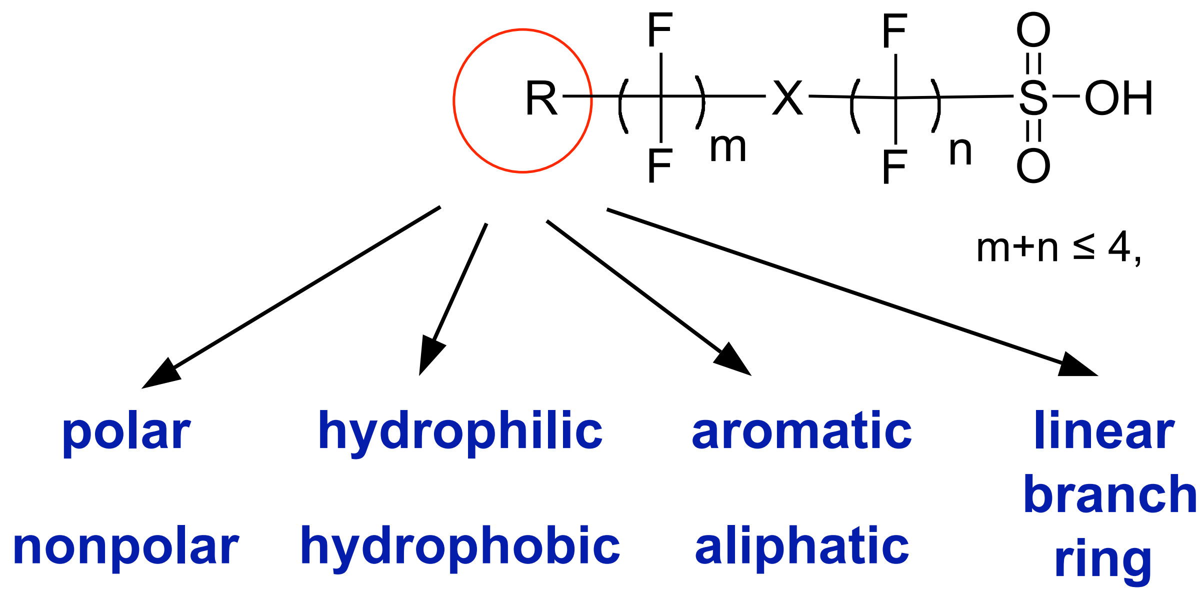
RBS Depth Profile of polar PAGs in a IBMA-MMA-MAA-t-BMA matrix



NEXAFS spectra of polar PFOS in a IBMA-MMA-MAA-t-BMA matrix

C.K. Ober et al., *JPST* (1999); J. L. Lenhart et al., Langumir, (2005); W. Hinsberg et al., SPIE, 2004; M. D. Stewart et al., *JVSTB* (2002)

Molecular Design of New Acids: Environmentally safe, Better Performance

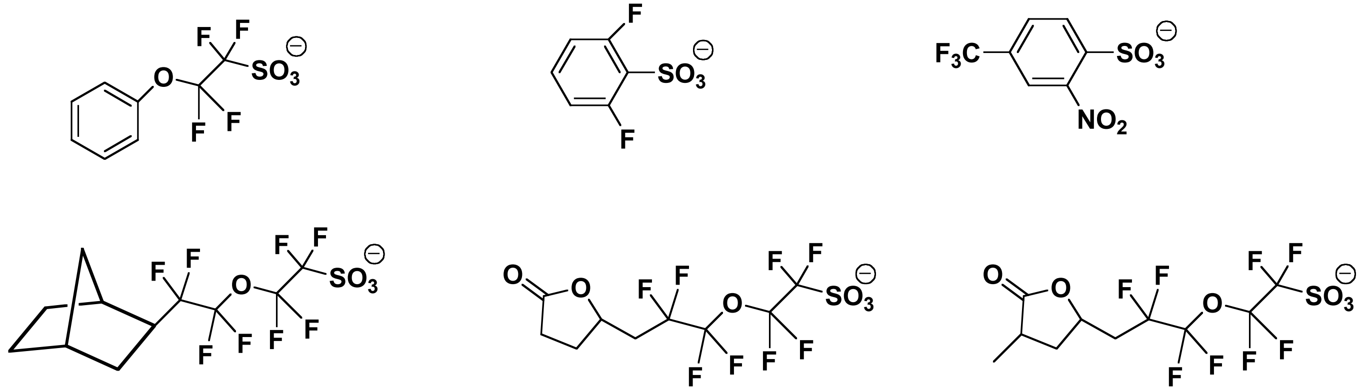


Practical synthetic chemistry considerations:

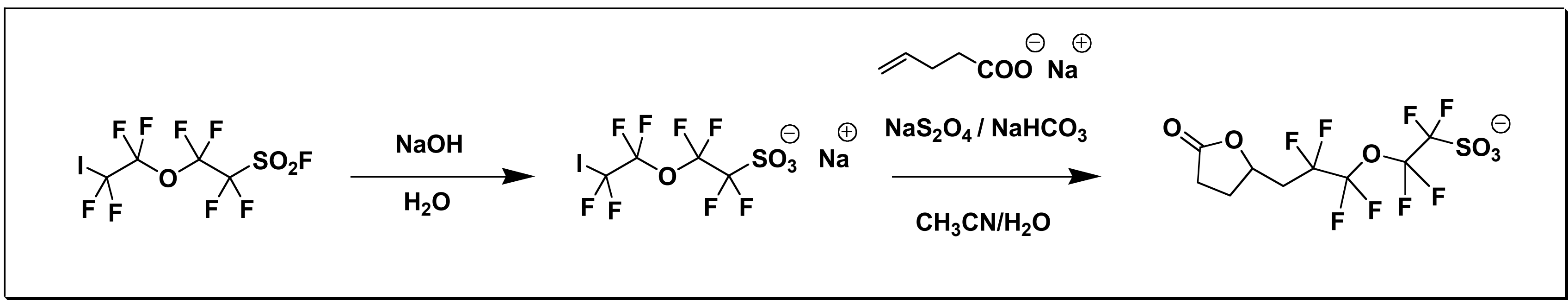
- Simple chemistry — low cost & less time
- Efficient reactions — high yield & high purity

New non-PFOS PAG Anions

Selected examples:

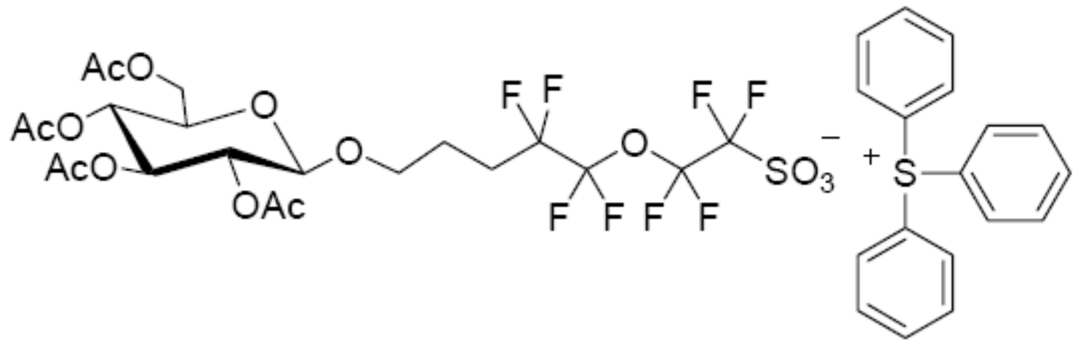


Synthetic scheme of a PAG anion:

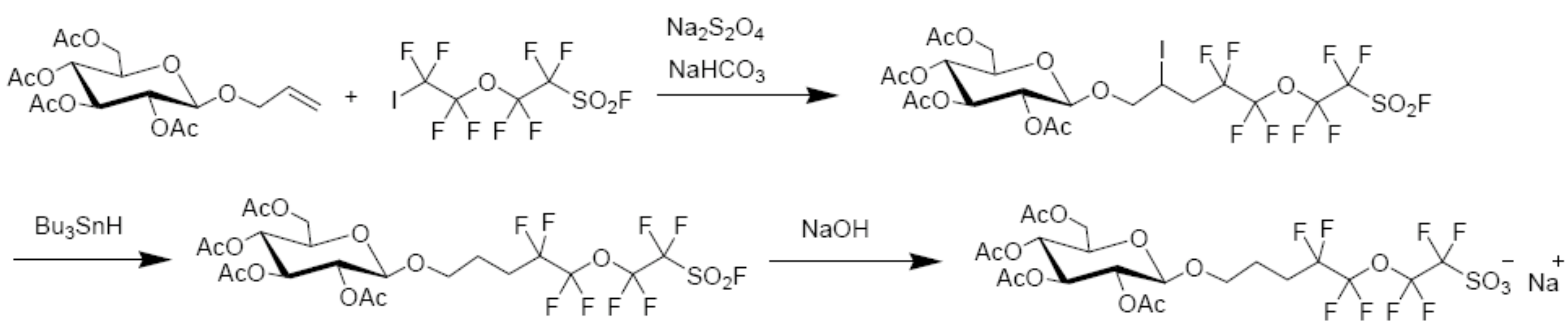


Synthesis of "Sweet" PAG

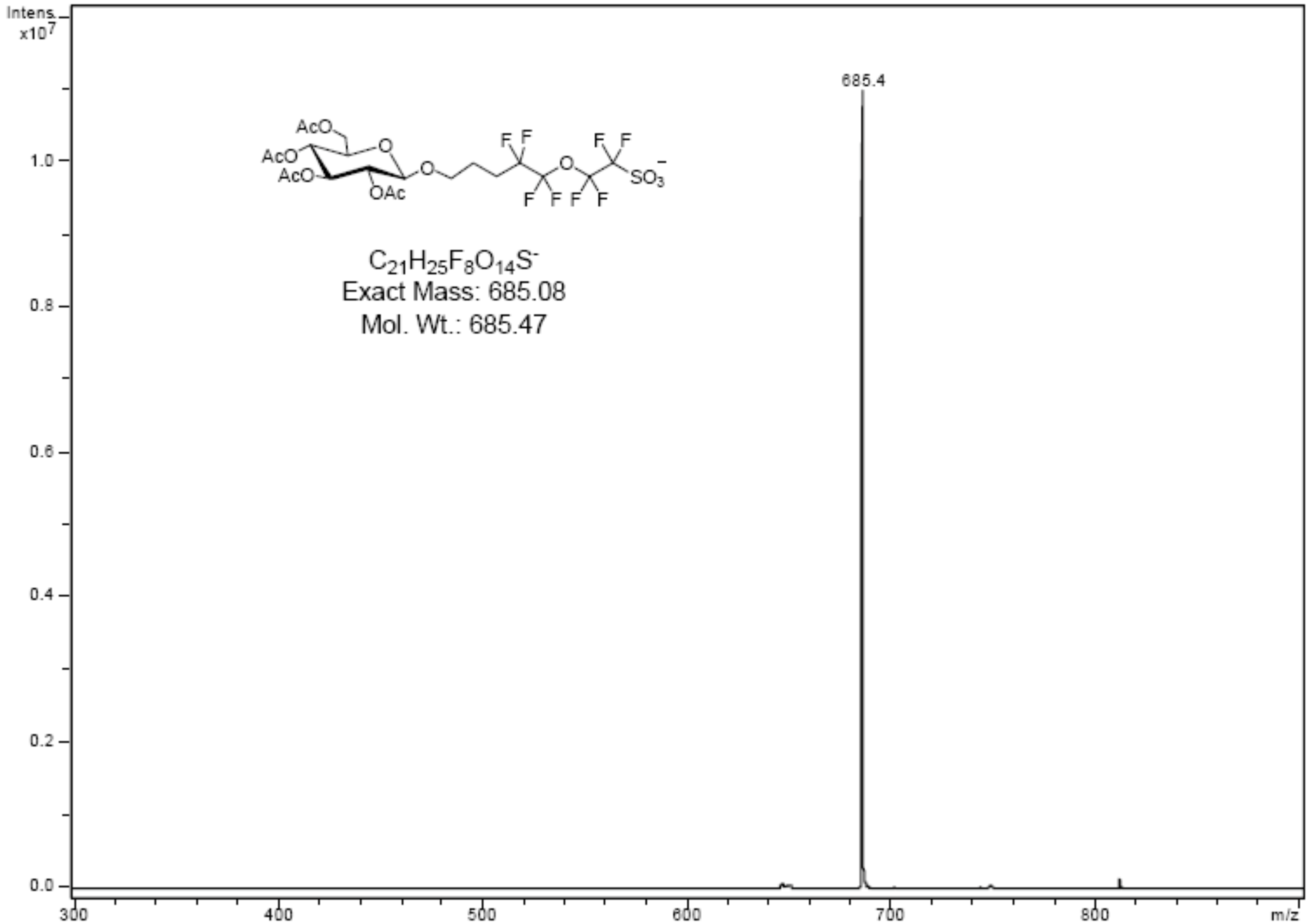
Final structure:



Synthetic Scheme:

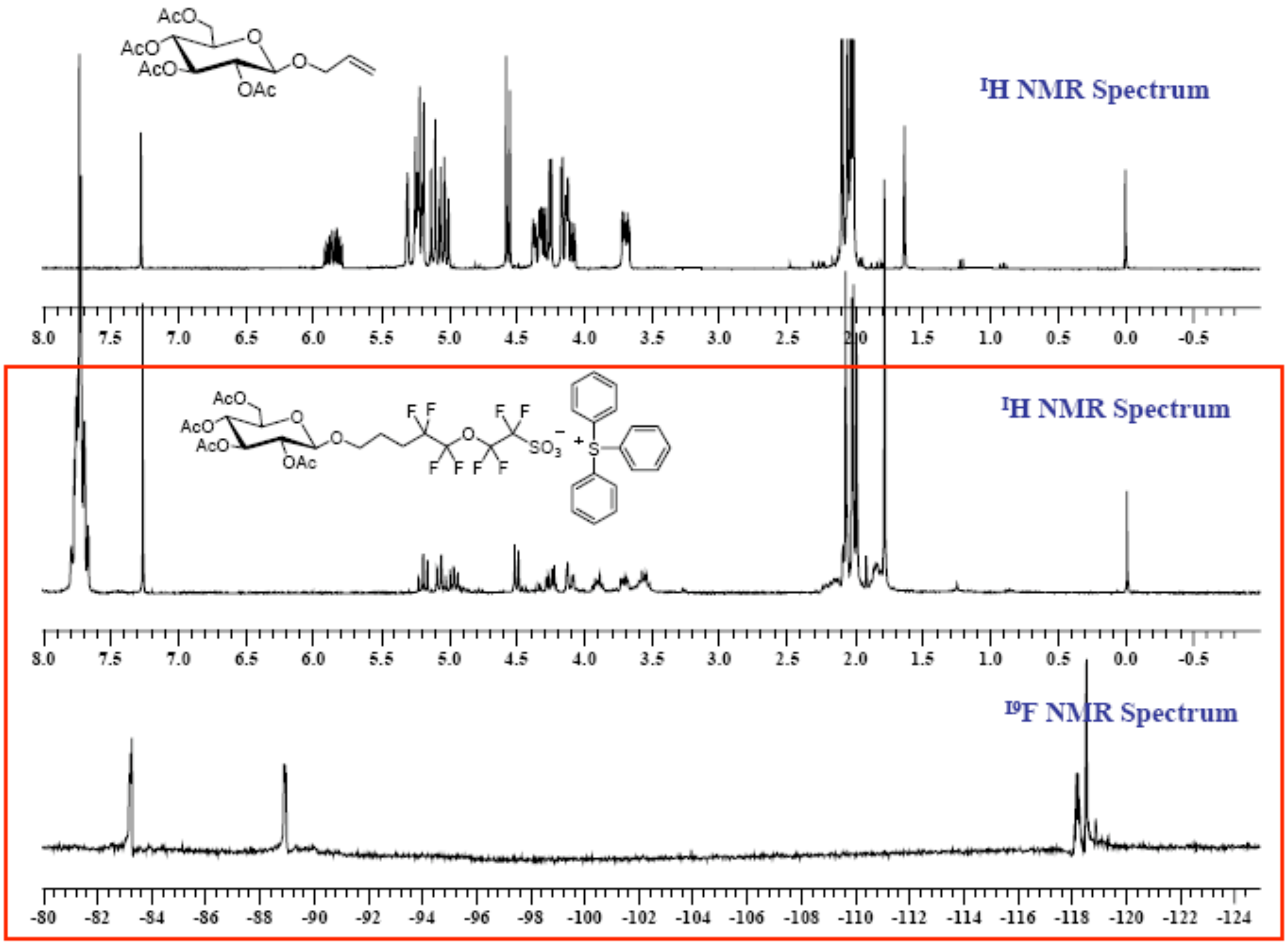


High Purity Sweet PAG (via MS)

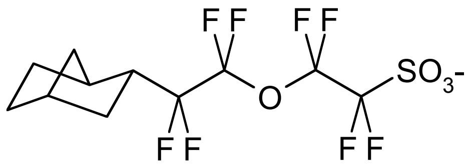


SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

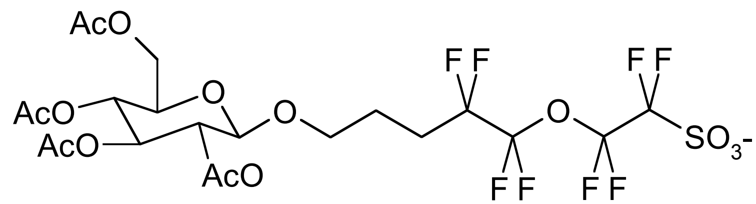
Characterization of Sweet PAG



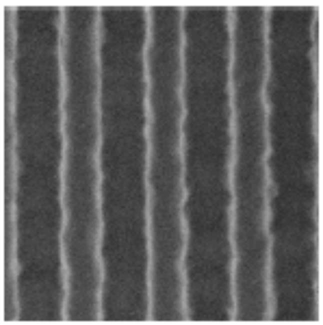
Evaluation of Lithographic Performance



NBPFEES (NB)



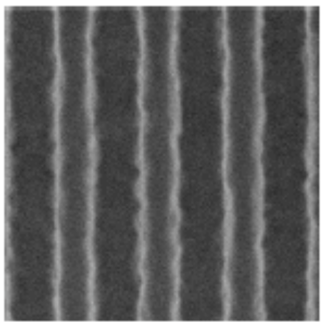
Sweet PAG (Sweet)



TPS-NB

90.8nm @ 23.8mJ/cm²

LER: 5.8±0.4



TPS-Sweet

92.2nm @ 27.3mJ/cm²

LER: 6.5±0.4

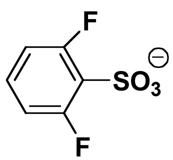
PAG	Esize@Target	MEF	EL by +/- 10% of target CD
TPS-NB	25.48	3.18	12.94
Sweet PAG	49.78	3.20	12.90

MEF (Mask Error Factor. The lower, the better)
EL (Exposure latitude. The higher, the better)

Collaboration with Rohm & Haas

Environmental Compatibility of New Non-PFOS PAG Anions

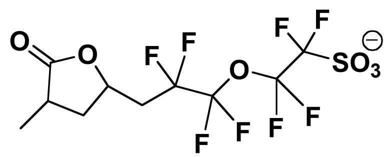
Selected examples:



PAG-1

1^{st} generation PAG

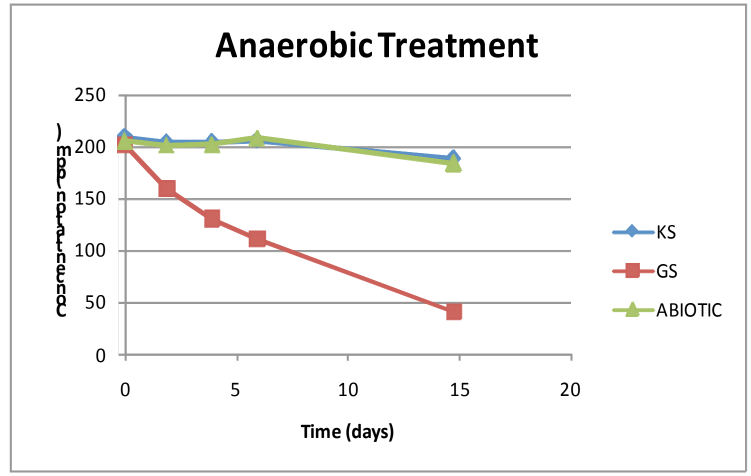
(Aromatic structure)



PAG-2

2^{nd} generation PAG

(Aliphatic structure)

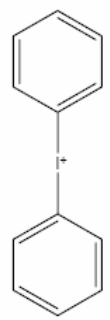


Degradation for PAG-2 in anaerobic batch bioassays. (KS) Abiotic sterilized control; (GS) complete treatment with active sludge; (ABIOTIC) sterile, non-inoculated control.

- **1^{st} Generation Non-PFOS PAGs: Low toxicity and low bioaccumulation potential, but relatively persistent to microbial degradation.**
- **2^{nd} Generation Non-PFOS PAGs: Preliminary results show that replacing the phenyl group with a UV-transparent alicyclic moiety increases the susceptibility of the PAG compound to biodegradation.**

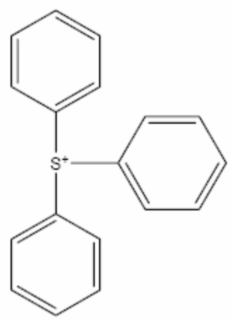
Environmental Compatibility of PAG Counterions

Selected examples of common PAG counterions:



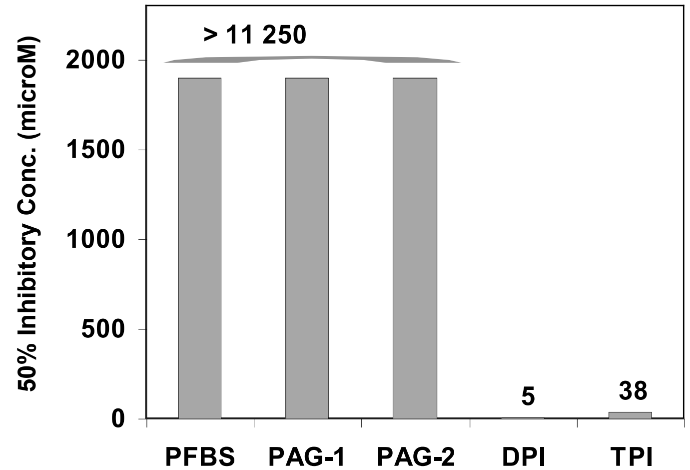
Diphenyliodonium

(DPI)



Triphenylsulfonium

(TPI)



Toxic response of the new PAG anions and selected PAG counterions in the Microtox assay. The most toxic compounds are those with the lowest inhibitory concentrations.

- **DPI and TPI should be replaced by more benign alternatives. Both counterions were highly toxic in assays with microbial and human cells.**
- **The EPA environmental compatibility software, PBT *Profiler*, estimated that triphenylsulfonium may be a PBT (persistent-bioaccumulative-toxic) pollutant.**

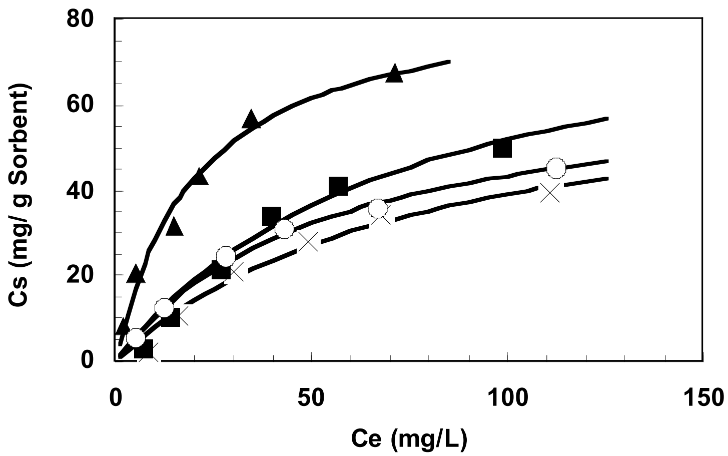
Treatability of New Non-PFOS PAG Anions (1st generation compounds)

The new non-PFOS PAG anions (1st generation) are amenable to removal by several physico-chemical treatment methods

- **Activated carbon adsorption**: PAGs can be removed with activated carbon. Adsorption increased with increasing side chain length.

- **Advanced chemical oxidation** (Fenton's reagent): Very efficient in the removal of new PAGs. PFOS and PFBS are recalcitrant to oxidative attack.

- **Chemical reduction with zero-valent iron:** Low or no removal of new PAGs, PFOS and PFBS.



Comparison of non-PFOS PAG adsorption on activated carbon. (X) PAG-1; (○) PAG-2; other first-generation non-PFOS PAGs: (▲) SF2; (■) PF1; Continuous lines show the fitting of the isotherm data to the Langmuir model.

Industrial Interactions and Technology Transfer

- Samples provided to Rohm & Haas Electronic Materials
- Collaboration with Rohm & Haas Electronic Materials for photolithography tests of Sweet PAG
- Samples provided to TOK
- Samples provided to AZ Microelectronics
- Performance at 193 nm and EUV evaluated with the assistance of International Sematech and Albany Nanotech
- Interactions with Intel on LER issues

Task Deliverables

- **Report on the completion of testing of new PFOS-free photoacid generators for 193 nm and EUV performance (Dec 06)**
  - ***completed***
- **Report on the assessment of the environmental compatibility of new PFOS-free photoacid generators. (Dec 07)**
  - ***completed***
- **Report on the completion of testing to determine the removal of PFOS-free photoacid generators by biological and physico-chemical treatment methods. (May 08)**
  - ***completed***
- **Report on new PFOS-free PAGs with improved performance and improved environmental impact. (Mar 09)**
  - ***On schedule***

Future Plans

Next Year's Plans

- Prepare next generation sugar-based Sweet PAG
- Reduce synthetic steps and use more environmentally friendly chemicals
- Environmental evaluation of the new Sweet PAGs
- Summarize previous studies and submit manuscripts for transfer of know-how to technical community

- More details during discussion of new projects

Publications, Presentations, and Recognitions/Awards

Publications

- **Ayothi R., Yi Y., Cao H. B., Wang Y., Putna S., Ober C. K. "Arylonium Photoacid Generators Containing Environmentally Compatible Aryloxyperfluoroalkanesulfonate Groups" *Chem. Mater.* 2007, 19, 1434.**
- **Yi, Yi; Ayothi, Ramakrishnan; Ober, Christopher K.; Yueh, Wang; Cao, Heidi. Ionic photoacid generators containing functionalized semifluorinated sulfonates for high-resolution lithography. Proceedings of SPIE (2008), 6923 69231B-69231B-8.**
- **Yi Yi, Ramakrishnan Ayothi, Yueh Wang, Mingqi Li, George Barclay, Heidi Cao and Christopher K. Ober, "Ionic Photoacid Generators for 193 nm & EUV Lithography", *J. Mater. Chem*., in preparation.**

Presentations

- **IBM Self-assembly Workshop, Almaden, CA, Jan. 15, 2008. "Photopatternable Block Copolymers: Chemically Active BCP Resists", invited talk.**
- **SPIE Conference, San Jose, CA, Feb. 26, 2008. "New Architectures for High Resolution Patterning"**
- **Sematech Workshop on Approaching the Optical Limit, Sagamore Hotel, Bolton Landing, NY, May 15, 2008. "LCAR 193nm Resists", invited talk with Bruce Smith (RIT)**
- **Rochester Institute of Technology, Rochester, NY, Oct. 22, 2008. "New Approaches to Sub-50 nm Lithography: Molecular Glasses and Block Copolymers", invited talk.**
- **CNMS Discovery Lecture Series, Oak Ridge National Laboratory and University of Tennessee, Knoxville, TN, Dec. 5, 2008. "Rethinking Photoresists: New Approaches to Making Very Small Structures", invited talk.**

Students on Task 425.013

- Graduated Students and Current Affiliation
  - Nelson Felix, AZ Microelectronics, Dec 2007
  - Victor Pham, JSR Microelectronics, May 2004
- Current Students and Anticipated Grad Date
  - Victor Gamez, March 2009
- Internships (Task and related students)
  - Katy Bosworth, IBM
  - Evan Schwartz, Intel
  - Anuja de Silva, IBM