

Fluorous Related Presentations
The 235th ACS National Meeting, New Orleans, LA, April 6-10, 2008

[CHED 1312 - Oxygen dissociation from red blood cells in a perfluorocarbon solution](#)

Adam J. Hayek, Adam.Hayek@loras.edu, Department of Biochemistry, Loras College, 1450 Alta Vista Street, Dubuque, IA 52001, David J. Oostendorp, david.oostendorp@loras.edu, Department of Chemistry, Loras College, 1450 Alta Vista, Box 157, Dubuque, IA 52001-0178, and David Speckhard, Department of Chemistry and Biochemistry, Loras College, 1450 Alta Vista, Dubuque, IA 52001.

Using visible and near infrared spectroscopy to investigate the effects of a perfluorocarbon solution on the dissociation of oxygen from purified bovine red blood cells. Primarily, the oxygen dissociation curve of bovine red blood cells is found in a phosphate buffer solution through tonometry and then compared to known values. Next, the phosphate buffer solution is replaced by an isotonic and pH buffered perfluorocarbon solution. This perfluorocarbon solution will closely represent a new blood replacement therapy. The two oxygen dissociation curves are then compared and contrasted.

[Undergraduate Research Poster Session: Medicinal Chemistry](#)

2:00 PM-4:00 PM, Monday, April 7, 2008 Morial Convention Center -- Hall A, Poster

[COLL 238 - Synthesis and tuning of bimodal mesoporous silica by combined hydrocarbon/fluorocarbon surfactant templating](#)

Stephen E. Rankin, srankin@engr.uky.edu¹, Rong Xing, xing@chbmeng.ohio-state.edu², Barbara L. Knutson, bknutson@engr.uky.edu¹, and Hans-Joachim Lehmler, hans-joachim-lehmler@uiowa.edu³. (1) Department of Chemical & Materials Engineering, University Of Kentucky, 177 Anderson Hall, Lexington, KY 40506-0046, (2) Department of Chemical and Biological Engineering, Ohio State University, 125 Koffolt Laboratories, 140 West 19th Ave, Columbus, OH 43210, (3) Department of Occupational and Environmental Health, University of Iowa, 100 Oakdale Campus, #124 IREH, Iowa City, IA 52242

Hydrocarbon and fluorocarbon surfactants show highly nonideal mixing that under some conditions results in demixing of the two types of surfactants into distinct populations of fluorocarbon-rich and hydrocarbon-rich aggregates. This also occurs in materials prepared by cooperative assembly of hydrolyzed tetraethoxysilane with mixtures of cetyltrimethylammonium chloride (CTAC) and 1,1,2,2-tetrahydro-perfluorodecylpyridinium chloride. Here, we demonstrate conditions under which demixed micelles lead to bimodal mesoporous materials (including the concentrations of ammonia and salt in the synthesis solution), and show that the hydrocarbon-templated and fluorocarbon-templated pores can be finely and independently controlled by adding lipophilic or fluorophilic oils, respectively. Nitrogen sorption isotherms and transmission electron microscopy provide clear evidence for a single phase of demixed but disordered wormhole-like pores

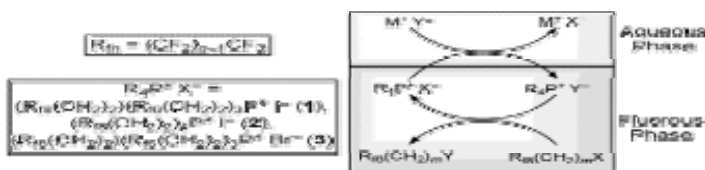
[Fundamental Research in Colloid and Surface Chemistry](#)

6:00 PM-8:00 PM, Monday, April 7, 2008 Morial Convention Center -- Rm. 244/245, Poster

[FLUO 9 - Fluorocarbon microenvironments and phases for catalyst activation and recovery](#)

John A. Gladysz, gladysz@mail.chem.tamu.edu, Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842-3012

Fluorous catalysis has primarily been regarded as a method for catalyst recovery, and recent advances involving fluoropolymer solid phases will be highlighted. However, it seemed to us that fluorous techniques might also be used for catalyst activation. For example, there are many metal-based catalyst precursors from which a ligand must first dissociate before the catalytic cycle can be entered. The reverse reaction often slows the overall rate. Thus, if the ligand could be efficiently scavenged, faster reactions would occur. This presentation will detail the synthesis of analogs of Grubbs' second generation catalyst with fluorous phosphines, and their application in metathesis reactions in organic solvents and fluorous/organic liquid/liquid biphasic systems. Under the latter conditions, significant rate accelerations are observed, consistent with a lower concentration of phosphine in the reactive phase. In a related endeavor, we were curious whether reactions involving ions might be possible in fluorous solvents. Scenarios are easily envisioned whereby it would be desirable to carry out a range of reactions in a fluorous phase. Towards this end, the synthesis and physical properties of fluorous phosphonium salts will be reported. These serve as phase transfer catalysts for Finkelstein-type displacement reactions in fluorous and other non-polar media.



[Fundamental Research in Colloid and Surface Chemistry](#)

6:00 PM-8:00 PM, Monday, April 7, 2008 Morial Convention Center -- Rm. 244/245, Poster

[PMSE 93 - Surface modification by fluorous polyoxetanes and polyurethanes](#)

Ying Zheng, yzheng@vcu.edu and **Kenneth J. Wynne**, Department of Chemical and Life Science Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, VA 23284

We discuss polyoxetane [poly(1,3-propylene oxide)] surface science involving polyurethanes with P[AB]-*co*-polyoxetane telechelics as soft blocks and semicrystalline fluorous polyoxetanes. Homo- and *co*-polyoxetane telechelics were synthesized by cationic ring opening polymerization of 2, 2-substituted oxetanes. Amorphous P[AB]-*co*-polyoxetane telechelics were incorporated into polyurethanes as soft blocks, which resulted in interesting surface properties due to synergistic interactions between **A** and **B** side chains. Semicrystalline poly(bistrifluoromethyl) oxetanes showed process dependent surface topology and time-dependent water contact angles due to crystallization and concomitant formation of sharp micrometer-scale ridges and asperities.

[Polymer Surfaces and Interfaces -- Loops, Branches and Brushes](#)

8:00 AM-12:10 PM, Monday, April 7, 2008 Hilton New Orleans Riverside -- Grand Salon 21, Oral

[FLUO 10 - Fluorous-based tools for glycomics](#)

Nicola L. Pohl, npohl@iastate.edu, Department of Chemistry and the Plant Sciences Institute, Iowa State University, Gilman, Ames, IA 50011

Genomics and proteomics have been aided significantly by automated solid-phase synthesis of nucleic acids and peptides. Unfortunately, solid-phase synthesis usually requires large excesses of building blocks to achieve the high yields needed when intermediates cannot be purified and therefore is practically limited to building blocks that are made in a few steps. This talk will discuss an alternative solution-phase automation strategy to iterative synthesis that is based on fluorocarbon tags and the interface of this fluorous synthesis strategy with the formation of small molecule microarrays. Both qualitative and quantitative analyses of binding interactions with this noncovalent microarray platform in the context of carbohydrate-protein interactions will be presented.

[ACS Award for Creative Work in Fluorine Chemistry: Symposium in Honor of Dennis P. Curran](#)

8:30 AM-11:30 AM, Monday, April 7, 2008 Morial Convention Center -- Rm. 217, Oral

[POLY 309 - Synthesis and surface properties of a fluorous semicrystalline polyoxetane](#)

Kenneth J. Wynne and **Ying Zheng**, yzheng@vcu.edu, Department of Chemical and Life Science Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, VA 23284

Poly(bis-trifluoroethoxymethyl)oxetane, P(B-3FOx), $M_n = 21$ kDa, was prepared by a modification of conventional cationic ring opening polymerization. At ambient temperature the polymer is between T_g (-39 °C) and T_m (-70 °C). Tapping Mode Atomic Force Microscopy (TM-AFM) revealed an interesting process-dependent topology. Coatings that were melted and slow-cooled displayed increasing roughness over the course of 4-6 weeks at 25 °C. The result was a topology characterized by sharp micron scale ridges and asperities. The heat of fusion increases from an initial value of 21.9 J/g after slow cooling (non-isothermal melt crystallization) to 28 J/g after 6 weeks (non-isothermal melt crystallization plus isothermal melt crystallization). The coating appearance changes from transparent with a slight haze to translucent. The changing topology was accompanied by a spontaneous increase in contact angle (104 to 136° plus/minus 4°) which is attributed to an asperity-rich surface yielding a discontinuous three-phase contact line and to a change in the proportions of crystalline and amorphous area fractions accompanying crystallization.

[ACS Award in Polymer Chemistry: Symposium in Honor of James McGrath](#)

2:00 PM-5:00 PM, Monday, April 7, 2008 Hilton New Orleans Riverside -- Grand Salon 9/12, Oral

[FLUO 11 - Fluorous Chemistry in Pittsburgh: 1994-2008](#)

Dennis P. Curran, curran+@pitt.edu, Department of Chemistry, University of Pittsburgh, Chevron Science Center, 219 Parkman Avenue, Pittsburgh, PA 15260

This lecture will provide an overview of the fluorous chemistry that has been developed at the University of Pittsburgh, unified by the theme of strategic synthesis and separation. Separation techniques include liquid-liquid extraction, solid-liquid extraction and chromatography over fluorous silica gel. Featured are fluorous monophasic, biphasic and triphasic reactions along with the use of fluorous reagents, reactants, scavengers and protecting groups in traditional, solution phase parallel and mixture synthesis. The ease of separation and product recovery make fluorous methods attractive for large scale chemistry while their speed and reliability are strong assets for small scale chemistry. Work with new fluorous solvents and new directions in biomolecule synthesis and separation will also be highlighted.

[ACS Award for Creative Work in Fluorine Chemistry: Symposium in Honor of Dennis P. Curran](#)

8:30 AM-11:30 AM, Monday, April 7, 2008 Morial Convention Center -- Rm. 217, Oral

[PMSE 171 - Contrasting thermal behavior and morphology of polyurethanes containing P\[AB\]-co-polyoxetane telechelics with fluorous A and oligoalkylether pendant B groups having random and block sequences](#)

Kenneth J. Wynne and Tomoko Fujiwara, tfujiwara@memphis.edu. Department of Chemical and Life Science Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, VA 23284

Exploration of P[AB]-soft block co-polyoxetanes and polyurethanes incorporating these soft blocks has led to several new surface phenomena including contraphilic wetting. In this work, using ring opening polymerization, polyoxetane [poly(1,3-propylene oxide)] telechelics with fluorous A and hydrophilic, oligoalkylether pendant B groups have been synthesized with random and block sequences. Polyurethanes incorporating these P[AB]-telechelics as soft blocks have also been prepared. DSC studies show identical Tg's for ran- and block-P[AB]-co-telechelics; the Tg's for ran- and block-P[AB]-soft blocks are also identical. However, TM-AFM reveals surface nanophase separation for the block-P[AB]-co-telechelic polyurethane, while the corresponding oxetane ran-P[AB]-co-telechelic polyurethane shows no surface microstructure. Interestingly, wetting behavior is influenced by the surface nanoscale morphology. This is the first time that the effect of soft block sequence distribution on polyurethane surface morphology and wetting behavior is demonstrated. Interestingly, the surface morphology is retained when the P[AB]-soft block polyurethanes are employed as surface modifiers (2 wt%).

[ACS Award in Applied Polymer Science: Symposium in Honor of Anne Hiltner](#)

8:00 AM-12:15 PM, Tuesday, April 8, 2008 Hilton New Orleans Riverside -- Grand Blrm C, Oral

[GEOC 77 - Sum-frequency spectroscopy of small molecule adsorption at fluorocarbon monolayer/water interfaces](#)

Adam Hopkins, ahopkins1@uoregon.edu, Chemistry, University of Oregon, 1253 University of Oregon, Eugene, OR 97403 and Geraldine L. Richmond, Department of Chemistry, University of Oregon, Eugene, OR 97403.

Fluorocarbon surfaces have been the subject of increasing study due to their importance in a variety of technological and biological processes. Understanding the molecular interactions of adsorbates at fluorocarbon/aqueous interfaces can provide insight into what makes fluorocarbon surfaces unique. To better understand these interactions, adsorption of simple amines, alcohols and water have been studied at fluorocarbon and hydrocarbon silane monolayer surfaces. Using vibrational sum-frequency spectroscopy, molecular orientation and adsorbate bonding have been measured for interfacial molecules.

[Advanced Approaches to Investigating Adsorption at the Solid-Water Interface](#)

8:20 AM-12:00 PM, Tuesday, April 8, 2008 Morial Convention Center -- Rm. 212, Oral

[FLUO 6 - Synthesis of oligosaccharide and peptide using heavy fluorous tag](#)

Mamoru Mizuno, mmizuno@noguchi.or.jp, Laboratory of Glyco-organic Chemistry, The Noguchi Institute, 1-8-1 Kaga, Itabashi-ku, Tokyo, 173-0003, Japan

A fluorous (highly fluorinated) solvent is immiscible in an organic solution, and a fluorous compound partitions out of an organic phase and into a fluorous phase. Therefore a fluorous compound is readily separated from nonfluorinated compounds by a simple "fluorous/organic" extraction. Curran and his co-workers elaborated the fluorous synthesis (fluorous-tag method) as a strategic alternative to solid-phase synthesis. The strategy of "fluorous synthesis" is designed to combine the advantages of solid-phase synthesis with those of traditional organic synthesis in the liquid-phase synthesis. Our group prepared some kinds of heavy fluorous tags, and reported that syntheses of oligosaccharides, peptides and glycopeptides were achieved efficiently. Recently, a new alkoxyphenyl fluorous tag was used in monosaccharides synthesis and oligosaccharide synthesis. In the synthesis of monosaccharide units, glycosyl acceptor and donor, the triple-chain fluorous tag enable easy purification of intermediates and final product using fluorous/organic extraction.

[ACS Award for Creative Work in Fluorine Chemistry: Symposium in Honor of Dennis P. Curran](#)

1:30 PM-4:50 PM, Sunday, April 6, 2008 Morial Convention Center -- Rm. 336, Oral

[BIOL 147 - Fluorous based peptide synthesis and immobilization in the formation of a protease microarray](#)

Tadamichi Nagashima, t.nagashima@Fluorous.com¹, Beatrice Collet², Marvin S. Yu, m.yu@fluorous.com¹, and Nicola L. Pohl, npohl@iastate.edu². (1) Fluorous Technologies, Inc, 970 William Pitt Way, Pittsburgh, PA 15238, (2) Department of Chemistry and the Plant Sciences Institute, Iowa State University, Gilman, Ames, IA 50011

Fluorous based synthesis, purification, and immobilization has been applied to the preparation of carbohydrate and small molecule microarrays. These microarrays have been shown to possess excellent spot morphology, high signal-to-noise, and low non-specific binding. They have also been validated to provide results consistent with other methods including SPR and chemical based assays. We now report the use of fluorous tags for the solution phase synthesis and purification of peptides followed by their direct spotting onto fluorous modified slides for microarray formation. In addition to demonstrating the viability of fluorous tags in peptide microarray formation this work also represents the first example of an enzyme assay based microarray on a fluorous surface. All previously reported fluorous microarrays were based on protein binding. Both N-termini and C-termini were fluorous tagged to determine the effect of peptide orientation in microarray performance. This work represents another step toward validating the use of fluorous techniques as a general immobilization technique in the formation of microarrays of various molecular classes.

[New Techniques in Chemical Biology](#)

9:00 AM-12:00 PM, Wednesday, April 9, 2008 Morial Convention Center -- Rm. 230, Oral

[BIOL 43 - Automated synthesis of hyaluronic acid and keratan fragments](#)

Beatrice Y. M. Collet, bcollet@iastate.edu and Nicola L. Pohl, npohl@iastate.edu. Department of Chemistry and the Plant Sciences Institute, Iowa State University, Gilman Hall, Ames, IA 50011

Hyaluronan and keratan are two important members of the glycosaminoglycan (GAG) family that are involved in a range of biological processes. To date, these highly functionalized saccharides are isolated from natural sources for use in the pharmaceutical industry. Their active structures still remain indeterminate. Consequently the possible "custom-made" automated synthesis of these macromolecules represents an extraordinary tool for biologists. Herein we present new methods for the synthesis of appropriate building blocks and programming of automation routines to assemble GAG fragments using a fluorocarbon tag for purification. We will present the scope and limitations of using fluorous solid phase extraction (FSPE) between reaction steps and when standard silica gel chromatography may be warranted in order to produce pure keratan and hyaluronic acid fragments useful for biological studies.

[Poster Session](#)

5:00 PM-7:00 PM, Tuesday, April 8, 2008 Morial Convention Center -- Hall A, Poster

[ORGN 229 - Automated solution phase synthesis of anthrax and cholera-associated antigenic tetrasaccharides](#)

Gisun Park, gsunny39@iastate.edu, Department of Chemistry, Iowa State University, Gilman Hall, Ames, IA 50011 and Nicola L. Pohl, npohl@iastate.edu, Department of Chemistry and the Plant Sciences Institute, Iowa State University, Gilman, Ames, IA 50011.

Although automated solid-phase synthesis for nucleic acids and peptides has been successful for decades, the same approach for oligosaccharide synthesis has lagged due to its lack of efficiency. Herein we present the first automated solution-phase method to synthesize two antigenic tetrasaccharides found on the surface of microorganisms that cause anthrax and cholera. The initial sugar monomers are attached to an alkene-containing fluoros tag for ease of purification by an incorporated automated fluoros solid-phase extraction (FSPE) routine. We will present the promise and limitations of how different solution phase chemistry conditions can be transferred to a fluoros-tag-based automation platform to assemble bioactive oligosaccharide structures.

[New Reactions and Methodology](#)

8:00 AM-12:00 PM, Monday, April 7, 2008 Morial Convention Center -- Rm. R04, Oral

[POLY 681 - Synthesis of regioregular amphiphilic PPEs](#)

Rakesh Nambiar, rakeshgatech@gmail.com¹, Kathy Woody¹, Joshua D. Ochocki, brown@southwestmsu.edu², and David M Collard, david.collard@chemistry.gatech.edu¹. (1) School of Chemistry and Biochemistry, Georgia Institute of Technology, MS&E Building, 9100 Atlantic Drive, Atlanta, GA 30332, (2) Science Department/Chemistry Program, Southwest Minnesota State University, 1501 State Street, Marshall, MN 56258

SYNTHESIS OF REGIOREGULAR AMPHIPHILIC PPEs

An understanding of the structure-property relationships of conjugated polymers is critical to the optimization of the behavior of these materials for use in microelectronics, energy storage, sensing and other applications. The interactions between side chains on the polymer backbone are of great importance in determining the supermolecular architecture of conjugated polymers. Poly(p-phenylene ethynylene)s, PPEs, are generally synthesized by Pd-catalyzed coupling reaction of diiodo (A-A type) and diethynyl (B-B type) monomers. With monomers bearing dissimilar alkyl or alkoxy substituents such polymerizations afford PPEs with an irregular substitution pattern of the side chains along the backbone. This hampers side chain crystallization and therefore affects molecular packing. We have developed a synthesis for the preparation of regioregularly-substituted PPEs by use of an A-B type iodo-ethynyl monomer. With installation of a combination of alkyl, oligo(ethylene glycol) and perfluoroalkyl substituents we have prepared amphiphilic materials that provide us with the opportunity to attain further control over the molecular architecture of this important class of conjugated polymers.

[General Papers](#)

1:30 PM-5:30 PM, Thursday, April 10, 2008 Hilton New Orleans Riverside -- Grand Salon 3/6, Oral