1st Workshop on Macromolecular Separations-by-Design
October 10th & 11th, 2012
Gaithersburg, Maryland, USA
October 10 – Statement of the Problem and State-of-the-Art

8:00-8:15  Arrive/Check-in, Administration Building - 101, Lecture Room B
8:15-8:30  Welcoming Remarks
8:30-9:00  Kate Beers, NIST. Introduction & Goals.

   *André Striegel, session chair*

9:00-9:40  Jimmy Mays, University of Tennessee. “Polymer Synthesis At and Beyond the Limits of Characterization: Limitations of SEC.”


10:20-10:35  Break

   *Catherine Rimmer, session chair*

10:35-11:15 Peter Schoenmakers, University of Amsterdam. “Towards HYPERformance polymer separations.”


11:55-1:00  Lunch, NIST Cafeteria

   *Karen Phinney, session chair*

1:05-1:45  Patricia Cotts, DuPont. “Characterization of functionalized nanoparticles for nanocomposite applications.” Lecture Room B


2:55-3:10  Break

   *Jack Douglas, session chair*

3:10-3:50  Karl Freed, University of Chicago. “Polymers in confinement.”


4:30-5:00  William Krekelberg, NIST. “A fundamental study of the conformational phase behavior of chain molecules at interfaces.”

6:00  Reception/Banquet, Gaithersburg Hilton
October 11 – Defining Challenges & Needs

8:30-9:00  Ming Zheng, NIST. “Structure-based Separation of Carbon Nanotubes.”
           Administration Building - 101, Lecture Room B
9:00-9:15  André Striegel, NIST. Breakout Session instructions.
9:15-10:30 Breakout Sessions

Please attend the session color coded on your badge
   Blue – Group A, Vincent Shen, facilitator – Dining Room A
   Orange – Group B, André Striegel, facilitator – Dining Room B
   White – Group C, Karen Phinney, facilitator – Lecture Room B
10:30-10:45 Break
10:45-11:00 Check-in, Lecture Room B
11:00-12:15 Breakout Sessions II, Lecture Room B, Dining Rooms A & B
12:15-1:15 Lunch, NIST Cafeteria
1:20-2:00 Present session results, Lecture Room B
2:00-3:30 Summary for Report
3:30     Workshop Ends

Thank you for the generous support of the workshop sponsors:
Polymer Synthesis At and Beyond the Limits of Characterization: Limitations of SEC

Jimmy Mays

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Size exclusion chromatography (SEC) has, over the past half-century, become the method of choice for characterizing molecular weights and molecular weight distributions of polymers and copolymers. The popularity of SEC in part reflects its simplicity and easy implementation; using only three solvents and commercially available columns, hardware, and software, almost any soluble polymer can be characterized. Advances in calibration methods and implementation of molecular weight/molecular size sensitive detectors have further entrenched SEC as the premier technique for polymer molecular weight determinations.

However, a number of recent studies on model polymers using new and powerful techniques, such as MALDI-TOF-MS and, especially, temperature gradient interaction chromatography (TGIC), reveal serious limitations of SEC as a method for characterizing polymers ranging from simple linear polymers made by anionic polymerization to complex copolymer architectures. In this presentation, I will review some of these limitations which are largely a consequence of three factors: the large band broadening effects in SEC, its inherently poor resolution, and the size-based separation mechanism.

Multiblock Polymers: New Opportunities and New Challenges

Timothy P. Lodge

Department of Chemistry and Department of Chemical Engineering & Materials Science
University of Minnesota

The ability of block copolymers to self-assemble into highly organized nanostructures is well established. Although simple “AB” diblocks have been studied extensively, and the rules governing the selection of morphology almost quantitatively established, this architecture is inadequate for many applications. For example, the most commercially successful block polymers to date are thermoplastic elastomers produced from ABA triblocks, in which the formation of a network structure (“A” crosslinks in a “B” matrix) confers substantial mechanical strength. Indeed, a simple argument based on chain bridging suggests that at least four blocks (ABAB…) are necessary to secure optimum toughness. Similarly, the desire to incorporate multiple functionalities into self-assembled materials has initiated extensive experimental explorations of ABC triblock terpolymers, as well as even more elaborate architectures. Significant advances in controlled polymerization technique have enabled preparation of almost any conceivable block polymer architecture. However, this synthetic flexibility immediately poses two questions: how does one decide what architecture to make, and how does one accurately characterize the material that has been made? In this talk examples of interesting multiblock architectures will be provided, and issues surrounding their characterization will be identified.
Towards HYPERformance Polymer Separations

Peter Schoenmakers

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Science Park 904, 1098 XH Amsterdam, The Netherlands

The prevailing trend in liquid chromatography is the progression towards smaller (sub-2 µm) particles and higher pressures (100 MPa or higher). We have come to use the designation ultra-high-performance liquid chromatography (UHPLC) for this mode of operation. Other important developments in LC include the use of monolithic and core-shell (superficially porous) particles. All these developments seem to be neglected in the field of polymer separations.

The main purpose of this lecture is to discuss whether and how developments in LC may be used in polymer separations. It will be demonstrated that UHPLC can have significant benefits for polymer separations. A greater choice of columns would be needed to make full use of these benefits. There also is a need for modifications in instrumentation, such as the detectors we like to use for characterizing polymers.

In one aspect polymer separations are very much at the front of developments in LC. This is the application of comprehensive two-dimensional liquid chromatography (LC×LC). Polymer samples are complex (many different molecules), but they have a low sample dimensionality (few parameters suffice to characterize the most-important differences between these molecules). Therefore, structured (LC×LC) chromatograms can often be obtained for synthetic polymers. It will be demonstrated that UHP (LC×LC) may lead to 10-fold shorter analysis times than conventional LC×LC.

Finally, it will be discussed how LC, LC×LC, and perhaps even LC×LC×LC of polymers may be taken to the next level, that of HYPERformance LC.
Chemical Composition and Microstructure Analysis of Complex Polymers by Multidimensional Liquid Chromatography

Harald Pasch, Pritish Sinha, Wolf Hiller

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1Technical University Dortmund, Faculty of Chemistry, Dortmund, Germany

Complex polymers are distributed in more than one direction of molecular heterogeneity. In addition to the molar mass distribution, they are frequently distributed with respect to chemical composition, functionality, and molecular architecture. For the characterization of such complex materials frequently multidimensional analytical methods are used.

Different liquid chromatographic techniques have been developed, including size exclusion chromatography (SEC) separating with respect to hydrodynamic volume, and liquid adsorption chromatography (LAC) which is selective towards chemical composition. Liquid chromatography at the critical point of adsorption (LC-CC) is a versatile method for the determination of the chemical heterogeneity of segmented copolymers.

The present talk presents the principle ideas of multidimensional analysis schemes for (block) copolymers. Most promising are the combination of two different chromatographic methods and the combination of chromatography and spectroscopy. The basic principles of two-dimensional chromatography and the hyphenation of liquid chromatography with selective detectors such as $^1$H-NMR will be discussed.

Various applications will be discussed showing the advantages of multidimensional chromatography and the on-line coupling of LC with $^1$H-NMR.

Characterization of Functionalized Nanoparticles for Nanocomposite Applications

Pat Cotts

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Realization of the potential attributes of nanocomposites has been limited by the inherent difficulty of dispersion. This has led to significant work in functionalizing the surface of the nanoparticles to improve interaction with the surrounding polymer. Characterization of the nanoparticles for size distribution is already challenging. Variations in surface functionality add another dimension to these challenges. We present examples of the use of chromatographic separations and light scattering to address these needs. Light scattering includes examples of intensity and dynamic light scattering, depolarized dynamic light scattering and zeta potential. Examples of nanoparticles include functionalized silica, TiO$_2$, and exfoliated clays such as sepiolite.
Challenges from an Industrial Perspective in the Molecular Structural Characterization of Polyolefins

A. Willem deGroot, Jeff Weinhold, Wallace Yau, and Ryan DePuit

The Dow Chemical Company
Freeport, Texas

In routine GPC, Triple Detector GPC, TGIC (Thermal Gradient Interaction Chromatography), and CEF (Crystallization Elution Fractionation), it is a general practice to rely on standards to calibrate our systems. Once our systems are calibrated it is common practice to proceed in running unknown samples and assume that the results will be of sufficient quality to solve a given problem. However, it is possible to take another step and apply model compounds to further evaluate the quality of our chromatography systems. By doing this we can potentially find and solve small problems in our system that we didn’t know existed or that we simply ignored in the past. Further, this information can give us confidence that ignoring known chromatography issues is a valid choice. For high temperature GPC, triple detector GPC and comonomer fractionation techniques, metalloocene polyolefins can make excellent model compounds. They are produced in the reactor in a very statistically predictable manner so simple mathematics can be used to describe their molecular weight distributions, their comonomer distributions and their long chain branching distributions. With this information in hand one can then compare the predicted results with the actual measured results to determine how well our system is performing. In this discussion, I will show several examples of how these model compounds have been used in our characterization ‘tool box’ at Dow to help us further understand how these techniques fractionate our polymers and how they can be used to further our knowledge of polymer molecular structure determination.
Design, Synthesis, and Characterization of Novel Hydrocarbon and Fluorocarbon Stationary Phases for Molecular Recognition in Liquid Chromatography

Catherine A. Rimmer, Lane C. Sander, Maximillian Kühnle, and Katrice A. Lippa

Chemical Sciences Division
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Gaithersburg, Maryland 20899

Alkyl modified silica surfaces are the most commonly used and studied bonded phases in liquid chromatography. The chromatographic effects of phase length, ligand density, and column temperature have been investigated extensively and it has been found that longer alkyl chains, higher densities, and lower temperatures typically lead to improved separations of shape constrained geometric isomers such as polycyclic aromatic hydrocarbons and carotenoids. In this presentation the design, synthetic preparation, and initial chromatographic and spectroscopic characterization of two novel classes of stationary phases will be described.

The novel materials were originally designed to possess a high degree of alkyl chain conformational order thereby enhancing their molecular shape recognition properties. Perfluorinated phases were synthesized via linkage of perfluorinated carboxylic acids of various lengths to alkylamino-modified silica particles. Longer chain perfluorinated sorbents display enhanced shape selectivity properties, even at elevated temperatures (70 °C). A series of C_{18} phases with various surface coverages were synthesized with deliberately introduced cavities through an initial reaction with a small monofunctional silane “spacer”, followed by reaction with octadecyltrichlorosilane via both solution- and surface-polymerization techniques. The presence of the spacer disrupts C_{18} ligand ordering and enhanced shape selectivity is observed for surface polymerized sorbents only. Evidence of stationary phase conformational ordering via solid state $^{13}$C/$^{29}$Si CP/MAS NMR and suspended state $^1$H HR/MAS NMR spectroscopy will also be presented.
Polymers In Confinement

Karl F. Freed

James Franck Institute and Department of Chemistry
University of Chicago, Chicago, IL 60637

All forms of chromatography involve methods in which polymer confinement governs the separation process, either by the partitioning of polymers between the free and confined regions in the limit of slow fluid flow or because of the difference in flow properties of polymers in these regions for processes with strong flow. The theoretical treatment of polymer partitioning between mobile and free regions has for the past 40+ years followed the classic methods of eigenfunction expansions and the use of long chain (ground state dominance). These eigenfunction methods encounter technical difficulties when considering the dependence on the full range of molecular weights, the influence of interactions with the confining surfaces, and the need to evaluate the average of flow properties, such as the drag force, over the configurations of the confined chains. We have implemented an alternative theoretical approach that utilizes Greens function methods and recent advances with numerical inverse Laplace transforms to approach problems of describing the influence of chain branching and polymer-surface interactions on the confinement probabilities, the analysis of a commonly used method for deducing pore sizes, and the recent methods introduced by Wu and coworkers for separating linear and branched chains.

Understanding Retention in Reversed-phase Liquid Chromatography and Size Exclusion Chromatography: Insights from Molecular Simulations

Ilja Siepmann

Department of Chemistry
University of Minnesota

Chromatographic separations involve a delicate interplay of enthalpic and entropic factors arising from interactions of the analyte molecules with the stationary and mobile phases, where the former can be altered by the presence of solvent (mobile-phase) molecules. Particle-based simulations allow one to probe chromatographic systems on the molecular level and to provide detailed information on structural characteristics and retention mechanisms. This talk will highlight recent applications of configurational-bias Monte Carlo simulations in the Gibbs ensemble to understand the retention mechanisms of small flexible analytes and of shape-constrained polycyclic aromatic hydrocarbons in reversed-phase liquid chromatography (RPLC) and of homo- and co-polymers in size exclusion chromatography (SEC). Accurate molecular mechanics force fields are used for the RPLC systems and enable direct comparison to experimental retention data, and the simulations elucidate the influence of mobile-phase composition, embedded polar groups, and grafting density for alkyl-silane based stationary phases. In contrast, simplified coarse-grain models are used for the SEC simulations and comparisons are made to theoretical predictions.
A fundamental study of the conformational phase behavior of chain molecules
at interfaces

W. P. Krekelberg and V. K. Shen

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National Institute of Standards and Technology
Gaithersburg, Maryland 20899

Chain molecules tethered or adsorbed to solid surfaces are at the heart of a wide range of
technologies. Examples include colloidal particle stabilization, chromatographic materials, and
drug delivery methods. Unfortunately, despite significant computational and theoretical efforts,
important fundamental questions remain. In particular, a basic understanding of how the
conformational phase behavior of tethered and adsorbed chain molecules depends on
thermodynamic constraints and surface chemistry is still lacking. In this talk, we
comprehensively study the conformational phase behavior of model homopolymers at solid
surfaces using advanced Monte Carlo simulation techniques that provide the free energy of the
system of interest to within an additive constant. We systematically determine how factors such
as chain length, chain density, and polymer-surface interactions impact the resulting structure of
adsorbed and tethered polymers. The properties of adsorbed and tethered polymers are
compared and contrasted to those of bulk polymer solutions.

Structure-based Separation of Carbon Nanotubes

Ming Zheng

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Carbon nanotubes (CNTs) can be regarded as a special type of polymers with many different
structural forms. Obtaining CNTs of well-defined structure has been one of the most challenging
issues in the field. To solve the problem, we have created a DNA-CNT hybrid whose structure is
dependent on both the DNA sequence and the atomic configuration of the encased CNT. In this
talk, I will show the use of conventional liquid chromatography tools to separate DNA-CNT
hybrids by nanotube’s chirality and length, and illustrate how the sorted CNTs enable
fundamental studies and application development.

References
3. Tu, X., Manohar, S., Jagota, A. & Zheng, M. DNA sequence motifs for structure specific
Macromolecular Separations Workshop
Breakout Discussion Topics/Notes

Group Spokesperson:
Facilitator:
Scribe:

MACROMOLECULAR SEPARATIONS

Critical Polymer Molecule Unknowns: Prioritization

- Quantifying Distributions
  - Architecture (Linear, Star, Branched, Cyclic)
  - Composition (statistical or block copolymers; blends?)
    - Charge/polyelectrolytes?
  - Mass (which descriptors? $M_n$, $M_w$, $M_v$?)
  - Other

- Rigidity/Aspect ratio /Persistence length?

- Functional assemblies/objects?
  - Supramolecular
  - Particles and rods/tubes
New Methods and Method Development

- Do you use/develop new methods?
  - 2D
  - Interactive
  - Gradient
  - Precipitation-redissolution

- If not, why?

- If so, which ones? What are the limitations? Advantages?

- What the bottlenecks in method development?
  - Solvent selection/mixed solvents
  - Availability/performance of stationary phases
  - Availability of specialized equipment
  - Software/data analysis
  - Other

Role of Models, Theory and Data

- Do you use Theory and Simulation tools in your process design and development for macromolecular characterization?
  - Why or why not?
  - How has it helped you?
  - What are the major challenges to adopting stronger connections between calculations and experiment (e.g. language barriers, complexity, etc.)?

- What are the major tools that you use?

- How could they be better?
Validation, Standards and Data

• How do you validate your data? Would best practice guides or different reference materials be important?

• What kinds of new standards would be most useful?

• Would data sharing resources, such as public databases or simply database frameworks, for separations or molecular characterization protocols or raw data that could be public or private be valuable to you?

Education, Training and Outreach

• Is your workforce adequately trained in polymer/macromolecule separation/characterization science?

• What technical skills are you looking for in new hires (PhD-level) in this general area?

• Are there critical educational/training resources that could be provided at the basic science, fundamental metrology level in new areas of separation science and molecular characterization?
  • e.g. Data (mis)interpretation

• Is there a center/facility or other resource an Institute like NIST could provide to accelerate adoption of new methods in industry?
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Find out more about us at www.polymerchar.com

MAIN SOLUTIONS

- **High Temperature GPC-IR**: The GPC-IR instrument is a reliable and fully automated 4D Gel Permeation Chromatography (GPC) system dedicated to the characterization of polyolefins. It incorporates the best infrared (IR) detectors, for the most comprehensive characterization of polymers such as HDPE, PP, LDPE, LLDPE, EP copolymers, EVA, EBA or others in the group of polyolefins, with the add-on of providing composition information as well.

- **CRYSTAF-TREF**: CRYSTAF-TREF is a completely automated apparatus for the analysis of the Chemical Composition Distribution in Polyolefins by CRYSTAF (Crystallization Analysis Fractionation) and TREF (Temperature Rising Elution Fractionation) techniques, providing a broad structural data base to improve catalyst knowhow and allowing new resins design.

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