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It is a pleasure to thank the following sponsors for their support of ISPAC 2013:

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- LG Chem
- PSS Polymer Standards Service
- Waters
- APMT Advanced Polymer Monitoring Technologies
- PolyRMC
- Tulane University
It is a pleasure to thank the following sponsors for their support of ISPAC 2013

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- Frontier Lab
- Metrohm USA
- Postnova Analytics
- Spectra Analysis Instruments
Welcome to New Orleans and the 26th annual International Symposium on Polymer Analysis and Characterization. We have worked hard to assemble a program of world renowned experts in the field and to attract many practitioners from industry, academia, and government. Participants come from all over the globe and we hope that each finds new colleagues, friends, and contacts, and takes back state-of-the-art knowledge that will broaden and deepen their own work. The program spends the first day on some of the most important spectroscopic and separation science methods in polymer analysis and characterization. The second day involves applications to the fields of therapeutic proteins, natural products, and novel polymeric systems. The final day moves on to rheological and modeling dimensions with numerous industrial applications. We hope you will both benefit from your participation in the scientific program and delight in the chance to explore a bit of New Orleans.

Wayne F. Reed
Dear Attendees and Guests of the ISPAC,

As Mayor of New Orleans, it is my pleasure to welcome you to our city for the 26th International Symposium on Polymer Analysis and Characterization (ISPAC), June 9-12, 2013. I want to thank you for your commitment to meeting in the Crescent City where you will experience the warm hospitality and unique culture of New Orleans.

I trust that New Orleans will serve as the perfect location for your symposia and will provide a great platform for extensive discussions and information exchange amongst your attendees. During the conference, I hope that the world’s leading experts in polymer analysis and characterization and all other participants take advantage of the many networking opportunities and learning experiences available. I’d like to thank our friends at Tulane University for their support.

I know that while you are here, you will embrace everything New Orleans has to offer. At the end of the day, take some time to relax, explore and dine in our incomparable restaurants, enjoy our great music scene, tour the historic French Quarter, and shop in our antique and specialty shops and boutiques throughout the community.

Again, thank you for choosing New Orleans. I hope you enjoy your stay and return often to our wonderful city.

Sincerely,

Mitchell J. Landrieu
Mayor
ISPAC Governing Board

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M. Rinaudo, CERMAV-CNRS, France; marguerite.rinaudo@esrf.fr
**G. J. Vancso, University of Twente, The Netherlands; G.J.Vancso@utwente.nl

* ISPAC Chair
** ISPAC-2012 Chair
*** ISPAC-2013 Chair

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S.T. Balke, University of Toronto, Canada
J.V. Dawkins, Loughborough University, UK
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Daniel Savin - University of Southern Mississippi (Hattiesburg, MS)
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Marco-Aurelio De Paoli - Unicamp (Campinas, Brazil)
Acknowledgements

The ISPAC organizers would like to thank all sponsors and exhibitors for their support of the symposium, as well as all invited speakers and governing board members for their contributions this year and in years past.

ISPAC would like to extend a special thank you to Tulane University for their support of this year’s symposium.

Finally, ISPAC organizers would like to thank Wayne Reed, Marissa Calko, Mike Drenski, Alex Reed, Christian Barker, Nick Chvany, Ryan Swinney, Sara Gottesman and Noelle and Cadie Higginson for all of their efforts in organizing the symposium.

Sponsored Scholarships

LG Chem Scholarship- David Norwood, Southeastern Louisiana University

Tulane University Scholarship- Boyu Zhang, Tulane University

Tulane-PolyRMC Scholarship- Colin McFaul, Tulane University

Polymer Char Scholarship- Xujun Zhang, Louisiana State University

Dow Chemical Scholarship- Apsana Shrestha, Southeastern Louisiana University

DuPont Scholarship- Kyle Bentz, University of Southern Mississippi

APMT Scholarship- Ryan Swinney, Tulane University
Sunday - June 9, 2013 - Vieux Carré Room

ISPAC Short Course on Polymer Analysis and Characterization

7:00am  REGISTRATION, ALL DAY

8:30am  Basics of Gel Permeation Chromatography, including Multi-detectors
Dr. John McConville, Polymer Standard Services, USA

10:00am  REFRESHMENT PAUSE

10:30am  Advanced Liquid Chromatography, including 2D-LC and Hyphenated Methods (LC-NMR, LC-FTIR, LC-MS)
Prof. Harald Pasch, University of Stellenbosch, South Africa

12:00pm  LUNCH (For Short Course Participants Only)

1:30pm  Characterization and Applications of Several Biopolymers
Prof. Marguerite Rinaudo, Joseph Fourier University, France

3:00pm  REFRESHMENT PAUSE

3:30pm-5:00pm  Introduction to Scattering-Based Polymer Characterization Methods
Prof. Paul Russo, Louisiana State University, USA

7:00pm-9:00pm  ISPAC RECEPTION (Light Refreshments and Drinks in the Riverview Room)
## Morning Session Theme: Polymer Separations and Chromatography

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<tr>
<th>Time</th>
<th>Event</th>
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<td>8:00am</td>
<td>REGISTRATION</td>
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<tr>
<td>8:20am</td>
<td>Opening Remarks</td>
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<tr>
<td>8:30am</td>
<td>Invited Lectures:</td>
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<tr>
<td></td>
<td>Coupling Techniques For Copolymer Characterization With Focus On LC-MS</td>
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<td></td>
<td>Prof. Jana Falkenhagen, Federal Materials Research Institute, Berlin, Germany</td>
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<tr>
<td>9:00am</td>
<td>HPLC Characterization Of Polymers Utilizing Isotope Effect</td>
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<td><em>The LG Chem Invited Lecture:</em> Prof. Taihyun Chang, Postech University, Pohang, Korea</td>
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<tr>
<td>9:30am</td>
<td>Characterization of Functionalized Nanoparticles for Nanocomposite Applications</td>
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<td><em>The Waters Corp. Invited Lecture:</em> Dr. Patricia Cotts, DuPont Central R&amp;D, Wilmington, Delaware</td>
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<tr>
<td>10:00am</td>
<td>DISCUSSION</td>
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<tr>
<td>10:45am</td>
<td>REFRESHMENT PAUSE</td>
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<tr>
<td>11:15am</td>
<td>Contributed Lectures:</td>
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<tr>
<td></td>
<td>Different Approaches for the Hyphenation of Size Exclusion Chromatography to Mass Spectrometry for the Structural Elucidation of (Co-)Polymers</td>
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<td></td>
<td>Prof. Clemens Schwarzinger, Johannes Kepler University, Linz, Austria</td>
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<tr>
<td>11:30am</td>
<td>Advances In Applications Of Polymer Characterization</td>
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<td></td>
<td>Mr. Jeremy Shia, Waters Corporation, Milford, Massachusetts</td>
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<tr>
<td>11:45am</td>
<td>Characterization Of Functional Poly(Ethylene Oxide)S And Their Corresponding Polystyrene Block Copolymers By Liquid Chromatography Under Critical Conditions In Organic Solvents</td>
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<td></td>
<td>Dr. Marion Rollet, University of Marseille / ICR-CROPS, France</td>
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<tr>
<td>12:00pm</td>
<td>Determination Of Polymer Composition And Composition Distribution By Thermal Field-Flow Fractionation</td>
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<td>Mr. Charles Ponyik, Colorado School of Mines</td>
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<tr>
<td>12:15pm</td>
<td>Ultra High Performance Size Exclusion Chromatography Of Synthetic Polymers</td>
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<td>Dr. Miroslav Janco, The Dow Chemical Company, Spring House, Pennsylvania</td>
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<tr>
<td>12:30pm</td>
<td>LUNCH (Poster Setup in Iberville Room)</td>
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## Afternoon Session Theme: Scattering and Spectroscopic Methods

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<td><strong>Invited Lectures:</strong></td>
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<td>2:00pm</td>
<td>Characterizing Polymers By Synchrotron X-Ray Radiation: Ideas, Trends And Opportunities</td>
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<td>Dr. Matthias Ballauff, Helmholtz Center for Materials and Energy, Berlin, Germany</td>
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<tr>
<td>2:30pm</td>
<td>Multi-Length Scale Morphology For Low Band Gap Polymer Photovoltaics</td>
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<td>Prof. Thomas Russell, University of Massachusetts, Amherst</td>
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<tr>
<td>3:00pm</td>
<td>Characterization Of Polyelectrolytes In Dilute Solutions: Light Scattering And Electrophysiology</td>
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<td><em>The APMT Invited Lecture:</em> Prof. Murugappan Muthukumar, University of Massachusetts, Amherst</td>
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<tr>
<td>3:30pm</td>
<td>DISCUSSION</td>
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<td>4:15pm</td>
<td>REFRESHMENT PAUSE</td>
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<td>4:45pm</td>
<td>Contributed Lectures:</td>
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<td>Equilibrium Kinetics In N-Alkane-PEO Micelles - A Time Resolved Sans Study</td>
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<td>Dr. Lutz Willner. Forschungszentrum Juelich, Germany</td>
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<td>5:00pm</td>
<td>Small-Angle X-Ray And Neutron Scattering Study Of A Protein-Cryoprotector System In Liquid, Supercooled Liquid, And Frozen States</td>
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<td>Mr. Arnold McAuley, Amgen Inc., Thousand Oaks, California</td>
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<td>5:15pm</td>
<td>Detection Of Polymer-Chain Branching In Complex Polymer Systems Including Linear Polymer Species</td>
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<td>Dr. Milos Netopilík, Akademia Nauk Ceske Republik</td>
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<td>5:30pm</td>
<td>Separation And Characterization Of Latex Particles By Asymmetric Flow Field Flow Fractionation And Dynamic Light Scattering</td>
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<td>Ms. Melissa Collins, Louisiana State University, Baton Rouge, Louisiana</td>
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<tr>
<td>5:45pm</td>
<td>Application Of Local Thermal Analysis In The Field Of Polymer Science</td>
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<td>Mr. Thomas Fischinger, Johannes Kepler University, Linz, Austria</td>
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<tr>
<td>6:00pm</td>
<td>Poster Exhibits and Refreshments in Iberville Room</td>
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Monday - June 10, 2013 - La Nouvelle Orleans West Room

Morning Session Theme: Polymer Separations and Chromatography

Contributed Lectures:

11:15am  Size-Exclusion Chromatography Of Ultrahigh Molecular Weight Cellulose Ethers For Accurate Molecular Weight Distribution Characterization  - Dr. Yongfu Li, The Dow Chemical Company, Midland, Michigan

11:30am  SEC-IR Coupled Technique To Characterize Polymer Grafting And Polymer Degradation  
Mr. William Carson, Spectra Analysis Instruments, Marlborough, Massachusetts

11:45am  Advances In SEC Analysis For Polymer Engineering Applications  
Dr. Michael O'Leary, Waters Corporation, Milford, Massachusetts

12:00pm  SEC-IR Hyphenated System For Characterizing Chemical Compositions Of Copolymers And Polymer Mixtures  
Dr. Ming Zhou, Spectra Analysis Instruments, Marlborough, Massachusetts

12:15pm  Advances In Polymer Characterization Using Multi-Detector GPC And Light Scattering  
Dr. Mark Pothecary, Malvern Instruments, Houston, Texas

12:30pm  LUNCH (Poster Setup in Iberville Room)

Afternoon Session Theme: Scattering and Spectroscopic Methods

Contributed Lectures:

4:45pm  Molecular Mobility In Polymers By Dynamic FT-IR Spectroscopy Using Continuous Scan Acquisition  
Dr. Sergey Shilov, Bruker Optics, Billerica, Massachusetts

5:00pm  Nanoscale Dynamic Mechanical Spectroscopy Of Polymer Blends And Composites  
Dr. Eoghan Dillon, Anasys Instruments, Santa Barbara, California

5:15pm  2D Chromatography And The Development Of Advanced Engineering Polymers  
Dr. Stephan Moyses, Sabic, Selkirk, New York

5:30pm  Characterization Of Morphology And Orientation Of Uniaxially Oriented Cast Films Confocal And Polarized M-Raman Imaging-Spectroscopy  
Dr. Krisztina Vincze-Minya, Johannes Kepler University, Linz, Austria

5:45pm  Surface Analysis And Characterization Of Plasma-Treated Polypropylene (PP) And Polyamide (PA) Films By Contact Angle Measurements, Scanning Electron Microscopy (SEM) And Atomic Force Microscopy (AFM)  
Mr. Ujjwal Joshi, Kathmandu U., Nepal

6:00pm  Poster Exhibits and Refreshments in Iberville Room
Tuesday - June 11, 2013 - La Nouvelle Orleans East Room

Morning Session Theme: Characterization of therapeutic proteins and delivery systems

Invited Lectures:
8:30am Quantifying Protein Interactions From "Low" To "High" Concentrations Using Complementary Scattering Techniques - The Biogen Idec Invited Lecture: Prof. Christopher Roberts, University of Delaware
9:00am Ensuring Accurate Size And Counts Of Protein Aggregates With Models And Reference Materials Dr. Dean Ripple, US Na'l. Inst. Standards & Technology (NIST), Gaithersburg, Maryland
9:30am High Resolution Characterization Of Proteins In Amorphous Solid Powders Prof. Elizabeth Topp, Purdue University, West Lafayette, Indiana
10:00am DISCUSSION
10:45am REFRESHMENT PAUSE

Contributed Lectures:
11:15am Investigating The Significance Of Submicron Particles For Protein Pharmaceutical Stability Dr. Mark Brader, Biogen Idec, Cambridge, Massachusetts
11:30am Surface Protein Adsorption Characterization By Quartz Crystal Microbalance With Dissipation (QCM-D): Case Studies - Dr. Sambit Kar, Pfizer, Inc., Chesterfield, Missouri
11:45am Use Of Simultaneous Multiple Sample Light Scattering (SMSLS) For Determination Of Equilibrium Properties And Aggregation Kinetics Of Protein - Prof. Wayne Reed, Tulane University, New Orleans, Louisiana
12:00pm Aggregate And Particle Analysis For Protein Therapeutics – Current Methods, Challenges And New Trends Dr. Alexandra Kafka, Coriolis Pharma, Munich, Germany
12:15pm Protein Quaternary Structure Characterization: The Effect Of Protein Self-Association On Analytical Method Development - Dr. Qin Zou, Pfizer, Inc., Chesterfield, Missouri
12:30pm LUNCH

Afternoon Session Theme: Current challenges in analysis and characterization for new polymers and natural products

Invited Lectures:
2:00pm Advanced Hydrogels: Design And Characterization The Tulane PolyRMC Invited Lecture: Prof. Tim Lodge, University of Minnesota, Editor, Macromolecules
2:30pm Application Of MALDI-TOF MS And IMS-MS For Elucidating Macromolecular Architecture The PSS Invited Lecture: Prof. Scott Grayson, Tulane University PolyRMC, New Orleans, Louisiana
3:00pm DISCUSSION
3:45pm REFRESHMENT PAUSE

Contributed Lectures:
4:15pm GPC And NMR Characterization Of A Lytic Copolymer Prof. Fabio Florenzano, UNIFAL-MG, Brazil
4:30pm pH-Responsive Amphiphilic Copolymers Via RAFT. Synthesis And Characterization Prof. Alina Alb, Tulane University PolyRMC, New Orleans, Louisiana
4:45pm Interfacial Curvature Effects In The Self-Assembly And Responsiveness In Polypeptide-Based Star And Triblock Copolymers - Dr. Daniel Savin, University of Southern Mississippi, Hattiesburg, Mississippi
5:00pm Countervailing Effects Of Ionic Strength And Composition On The Lower Critical Solution Temperature (LCST) Of Copolymers Of Poly(N-Isopropyl Acrylamide) And Acrylamide Mr. Colin Mcfaul, Tulane University PolyRMC, New Orleans, Louisiana
5:15pmSynthesis And Properties Of Biohybrid Glycopolymers And Chimeric Polysaccharides Capable Of Ionotropic Gelation - Prof. Marquerite Rinaudo, Joseph Fourier University (Grenoble, France)
5:30pm Abnormal Elution Of High Molecular Weight Polysaccharides Using Size Exclusion Chromatography Dr. Marie Dufrechou, CNRS / LoF Bordeaux, France
5:45pm Multiple-Particle Tracking Study Of The Microheterogeneity Of β-Glucan-Rich Hydrocolloidal Extractive Suspensions - Dr. Jingyuan Xu, NCAUR, ARS, USDA, Peoria, Illinois
7:30pm CONFERENCE BANQUET (Court of Two Sisters)
Tuesday - June 11, 2013 - La Nouvelle Orleans West Room

Morning Session Theme: Characterization of therapeutic proteins and delivery systems

**Contributed Lectures:**

**11:15am** Synthesis Of Polyhydroxyalkanoates (PHA) From Pseudomonas Aeruginosa, Using Glucose As A Carbon Source. An Alternative To Mitigate The Environmental Impact From CTSA Approach  
Mr. Michael Randle, Universidad Pedagógica Nacional de Colombia, Bogotá, Colombia

**11:30am** Polypeptides From Inside Out: Techniques For Investigating Their Dynamical Behavior And Properties  
Ms. Cornelia Rosu, Louisiana State University, Baton Rouge, Louisiana

**11:45am** Study Of The Mechanism Associated To The Mucoadhesion Phenomena In Polymers For Pharmaceutical Applications  
Dr. Jairo Perilla, National University of Colombia, Bogotá

**12:00pm** Customized Triglycerides For Polymer Synthesis  
Dr. H. N. Cheng, USDA Agricultural Research Service, New Orleans, Louisiana

Afternoon Session Theme: Current challenges in analysis and characterization for new polymers and natural products

**Contributed Lectures:**

**4:15pm** Characterization Of A New Sulfonated, High Temperature Polymer For Use In Hydrogen Fuel Cells  
Mr. David Randle, Diablo Analytical

**4:30pm** Stimuli Responsive Ultrahydrophobic Polymer Surfaces Synthesis, Characterization And Application  
Dr. Thorsten Hofe, PSS GmbH / Leibniz Inst., Dresden, Germany

**4:45pm** Determination Of Inorganic Elements In Brazilian Oxo-Biodegradable Plastics By Neutron Activation Analysis  
Mr. Mateus Boscaro, University of Sao Paulo, Brazil

**5:00pm** Utility Of Chromatographic And Spectroscopic Techniques For Detailed Characterization Of Complex Macromolecules  
- Dr. Ema Zagar, National Institute of Chemistry / Slov. Inst./King Abdul University, Saudi Arabia

**5:15pm** Characterization Of A Non-Ionic, Water Soluble, Helical, Rod-Like Polymer  
Mr. Wayne Huberty, Louisiana State University, Baton Rouge, Louisiana

**5:30pm** Understanding Branching Heterogeneity Of C60 Core Star Polymers By Temperature Gradient Interaction Chromatography  
- Dr. Dianna Pickel, Oak Ridge National Laboratory, Tennessee

**5:45pm** Original Mechanical Characterization Of Single Micrometric Vesicle By Atomic Force Microscopy  
Prof. Marguerite Rinaudo, Joseph Fourier University (Grenoble, France)
Wednesday - June 12, 2013 - La Nouvelle Orleans East Room

Session Theme: Modeling/computational approaches and comparison with experimental methods

Invited Lectures:

8:30am Inverting Models Of Polymer Rheology For Analysis And Characterization
Prof. Sachin Shanbhag, Florida State University, Tallahasee, Florida

9:00am The Structural Rheology Of Long Chain Branched Polymers - Measuring And Modelling Macromolecules In Flow
Prof. Tom McLeish, Durham University, UK

9:30am DISCUSSION

10:15am REFRESHMENT PAUSE

Contributed Lectures:

10:45am Investigating The Effects Of Supercritical Carbon Dioxide And Hydrogen Sulfide Mixes On The Morphology Of Polyphenylene Sulfide And A Fluoropolystyrene - Dr. Bernadette Craster, TWI Ltd., UK

11:00am Probing Industrial Polymer Compositions Using Liquid Chromatography Coupled To Infrared Spectroscopy Detection - Dr. Cherie Owens, Sabic, Selkirk, New York

11:15am Adaptation Of Automatic Continuous Online Monitoring Of Polymerization Reactions (ACOMP) to Industrial Scale Reactors - Mr. Michael Drenski, Advanced Polymer Monitoring Technologies, Inc., New Orleans, Louisiana

11:30am Inferring CCD Using Crystaf - Uncertainty Analysis
Mr. Arsia Takeh, Florida State University, Tallahasee, Florida

11:45am Detailed Characterization Of The Composition And Morphology Of Polystyrene-B-Poly(Ethylene Oxide)-B-Polystyrene Of Interest As Solid Electrolytes For Lithium Batteries
Ms. Berengere Pelletier, U. Marseille / ICR-CROPS, France

12:00pm Thermal Degradation Kinetics Of Un-Irradiated And High Energy Protons Irradiated Polyvinyl Butyral
Dr. Hassan Behnejad, University of Tehran, Iran

12:15pm Characterization Of Chemical Composition Heterogeneities In Polyolefins Using Two-Dimensional Liquid Chromatography With Online Infrared Absorbance Detector
Dr. Dean Lee, The Dow Chemical Company, Midland, Michigan

12:30pm Preparation And Characterization Of Swift Heavy Ion Beam Irradiated Polycarbonate/ Zinc Oxide Nanocomposites Films - Mulayam Gaur, Hind. Col. Sci. Tech, India
Contributed Lectures:

10:45am  Characterization And Comparative Study Of Polymers Used As Viscosity Index Improvers For Automotive Lubricant Oils - Prof. Maria Elisa Silva, *Federal University of Minas Gerais, Brazil*

11:00am  Rheological Characterization Of Gum Polymers Using Rotational And Oscillation Tests
Dr. Mar Nieto, *TIC Gums, Inc., White Marsh, Maryland*

11:15am  Blown Film Stability Of Bimodal Polyethylene Resins
Ms. Cecilia Treviño-Quintanilla, *Monterrey Tech., Mexico*

11:30am  Polyolefin Characterization By Diffusion Ordered NMR Spectroscopy
Dev Ranjan Pradhan, *Sabic, Saudi Arabia*

11:45am  Polyolefin Microstructure Analysis Via Triple Detector HT GPC Combined With FT IR Detection
Dr. Tianzi Huang, *The Dow Chemical Company, Freeport, Texas*

12:00pm  Application Of Malvern Polyolefin Characterization Technologies For The Process Control Of UHMW Polyethylene Resins And Fibers - Dr. Wei-Sen Wong, *Malvern Instruments, Westborough, Massachusetts*

12:15pm  The Development Of A Multi-Angle-Light-Scattering Detector For Characterization Of Proteins Macromolecules And Particles Using Either Field Flow Fractionation Or Size Exclusion Chromatography
Trevor Havard, *Postnova Analytics*

Short Course Abstracts
Basics of Gel Permeation Chromatography, Including Multi-Detectors

Dr. John McConville

Polymer Standard Services, Amherst MA

Abstract

An introduction to theoretical and practical aspects of GPC. Detailed discussion of GPC equipment (pumps, injection valves, detectors and other GPC instrumentation) will be presented. GPC columns, their performance characteristics and how to choose the right type and number of columns will be reviewed. The appropriate use of multiple detectors (refractive index, UV, viscometer, and multiple angle light scattering) will be reviewed and explained. Different methods for obtaining molecular weight distributions, beginning with traditional column calibration and proceeding through universal calibration and light scattering, which requires no calibration, will be covered. A brief overview of hyphenation in GPC (using FTIR, NMR and MS detectors) and 2-D techniques. Examples and applications including polyolefins, copolymers, aqueous polymers, etc. will be presented. Finally, an overview of common problems and troubleshooting will be given.
Advanced Liquid Chromatography, Including 2D-LC and Hyphenated Methods (LC-NMR, LC-FTIR, LC-MS)

Prof. Harald Pasch

University of Stellenbosch, South Africa

Abstract

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 the different types of molecular heterogeneity it is necessary to use a wide range of analytical techniques. Preferably, these techniques should be selective towards a specific type of heterogeneity. The combination of two selective analytical techniques is assumed to yield two-dimensional information on the molecular heterogeneity.

For the analysis of complex polymers 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 used to separate according to chemical composition. Liquid chromatography at the critical point of adsorption (LC-CC) has been shown to be a versatile method for the determination of the chemical heterogeneity of complex block and copolymers.

The present short course presents the principle ideas of combining different analytical techniques in multidimensional analysis schemes for complex polymers. Most promising protocols for hyphenated techniques refer to 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 1H-NMR, FTIR and MS will be discussed.
Characterization and Applications of Several Biopolymers

Prof. Marguerite Rinaudo

Joseph Fourier University (Grenoble, France)

Abstract

We will focus on water soluble polysaccharides; natural and modified polysaccharides will be considered to describe the main physical properties performed usually by polysaccharides in solution and gel states. Then, the main techniques used for their characterization will be discussed using several examples. Some applications will also be mentioned.

Systems considered: water soluble polysaccharides based on different types of monomeric units: anionic carboxylic uronic acid (as in pectins and alginates), glucosamine (as in chitosan) becoming cationic in acid medium, neutral sugar unit (glucose and galactose in galactomannans; methylated glucose in methylcellulose)

Polyelectrolyte behavior: Control of the purity of polymers and of the nature of counterion; Specific behavior of charged polymers in aqueous medium in viscometry and light scattering; Screening of long range electrostatic repulsions.

Prediction of the activity of mono and divalent counterions

Specific problems: Prevention of aggregation due to high yield of –OH monomeric units (H-bond network)

Stereo regularity, semi-rigid character and cooperativity of interactions

Polysaccharide investigated in this course:

Alginates (structure and gel characterization in acidic conditions and in presence of calcium; mechanism; application as biomaterial) (Main techniques: NMR, rheology)

Hyaluronan (conformation in solution, rheology in relation with molar mass and polymer concentration for viscosupplementation) (Main techniques: molecular modeling, NMR, SEC, rheology)

Chitosan (conformation in relation with the degree of acetylation; behaviour compared with that of hyaluronan; application as biomaterial). (Main techniques: molecular modeling, RMN, rheology, SEC)

Methylcellulose (example of amphiphilic system and mechanism of gel formation induced by temperature increase in relation with methyl substituents distribution along the cellulosic chain) (Main techniques: NMR, chromatography, DSC, rheology)
Introduction to Scattering-Based Polymer Characterization Methods

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Abstract

Determination of macromolecular and supramolecular structure in solutions, gels and solids can be challenging because the materials are often too soft for microscopic visualization at high resolution. Even when microscopy yields images without artifact, it can be tedious to examine a sufficient number of specimens, especially in polydisperse systems. In these cases, scattering of visible or X-ray radiation, or of neutrons, can be used to obtain quantitative information without bias and usually without artifact. Absolute molecular weights, particle sizes, extent of aggregation, stability, and phase behavior are just some of the problems that can be studied. Often scattering methods are coupled to on-line chromatographic separations, so that effectively monodisperse samples can be examined. In this short course, the essentials will be presented. Subjects will include scattering geometries, the scattering vector, angular dependence, particle sizes, correlation length and intensity fluctuations in time. Applications from the literature will illustrate these principles. A brief discussion of available instrumentation will round out the discussion.
Invited Lecture Abstracts
Coupling Techniques For Copolymer Characterization With Focus On LC-MS

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Abstract

Usually the characterization of complex polymers forces analytical chemists to apply more than one technique. The reason for that is the wide variety of molecular distributions existing simultaneously in a polymer sample. Systems are presented where different separation modes are linked and combined with multi-detector setups. The most sophisticated approach is the coupling of different modes of liquid chromatography in a so-called orthogonal two-dimensional (2D) way viz. two independent modes with completely different separation mechanisms (e.g. adsorption chromatography x size exclusion chromatography).

For the characterization of molecular structure of liquid chromatographic fractions MALDI-TOF-MS and ESI-TOF-MS are applied.

The pros and cons of both spectrometric techniques will be discussed for copolymer analysis. Finally, different LC-MS coupling principles will be compared. Examples containing biodegradable copolyester, star-shaped copolymers of polystyrene and polycaprolactone, or hyperbranched/dendritic polyesters are presented.
HPLC Characterization Of Polymers Utilizing Isotope Effect

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Abstract

Isotopes are chemically very similar in general but exhibit characteristic differences which can be effectively utilized in chemical analysis such as in NMR and neutron scattering. In addition, albeit it is less expected, isotopes exhibit a measurable difference in liquid chromatographic retention and it can be utilized to characterize complex polymers precisely, which cannot be done otherwise.

It is often claimed that a block in block copolymers can be made chromatographically “invisible” at the critical condition (compensation point of exclusion and interaction effect). Utilizing the “chromatographic invisibility”, liquid chromatography at critical condition (LCCC) has been used to characterize individual block in block copolymers. At the critical condition of A block, A block becomes “invisible” and A-b-B diblock copolymer elutes as if it is homo-B, and vice versa. Depending on the HPLC separation condition for the B block, A-b-B can elute in either SEC mode (elution before the injection solvent peak) or IC mode (elution after the injection solvent peak).

Even though the usefulness of LCCC has been well demonstrated in the characterization of block copolymers or functionality, the precision of individual block characterization of block copolymers has been under debate. The “chromatographic invisibility” is easy to check experimentally for the SEC mode elution, but practically impossible for the IC mode elution since the IC retention of polymer increases exponentially with molar mass in the isocratic/isothermal elution mode of LCCC.

Since the chromatographic retention difference between deuterated polystyrene (dPS) and normal polystyrene (hPS) is much smaller than (but distinctively different) a pair of different polymers in typical block copolymers, it was possible to elute the block copolymers at both exclusion and interaction regimes at the critical conditions of each block. We found that the block at its critical condition is not fully invisible at both cases. Nonetheless, the isotope sensitivity in LC retention can be utilized effectively to fully resolve the hPS-b-dPS diblock copolymers or hPS-g-dPS comb shaped polymers at near the critical condition of dPS at which hPS is slightly interactive.
Characterization of Functionalized Nanoparticles for Nanocomposite Applications

Patricia Cotts
DuPont

Abstract

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.
Characterizing Polymers By Synchrotron X-Ray Radiation: Ideas, Trends And Opportunities

Matthias Ballauff

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Abstract

Since a long time, scattering methods have been an indispensable tool in polymer science. Thus, small-angle X-ray scattering (SAXS) has been used e.g. for the elucidation of the structure of semicrystalline polymers or for analyzing polymeric micelles or supramolecular structures in solution. However, the information obtained by SAXS is very often too small to recover the full structure of the objects under consideration (inverse problem). Hence, additional information is needed for a correct reconstruction of the real-space structure. Recently, the advent of synchrotron radiation has led to entirely new opportunities for the analysis of polymers and to alleviate the inverse problem. In my lecture I shall focus on two subjects in this regard: 1. The use of anomalous small-angle X-ray scattering (ASAXS). ASAXS is using the anomalous dispersion of a given element in order to discern the scattering contribution from this element. In general, ASAXS leads to three partial intensities and thus triples the information of a conventional SAXS-experiment. The analysis of these partial intensities furnishes information not available by other methods [1]. 2. The combination of SAXS with cryogenic transmission electron microscopy (cryoTEM). Here the shape and the polydispersity of polymer colloids is analyzed by cryoTEM in real space while the fine structure is obtained from SAXS. We have shown that the combination of synchrotron-SAXS with cryoTEM is an excellent tool for the full elucidation of nanocrystals of polyethylene [2].

Multi-Length Scale Morphology For Low Band Gap Polymer Photovoltaics

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Abstract

Low band gap conjugated polymer bulk heterojunction solar cells have attracted much attention recently due to their promising application in fabricating high efficiency plastic solar cells. For many low band gap polymers, their device processing requires small amount of chemical additives to produce ideal phase separation. It has been shown that the chemical additive, usually a low vapor pressure solvent, could kinetically drive conjugated polymer to form crystals while keeping modified fullerenes, commonly used acceptor materials in the solubilized state. Further evaporation of additive molecules finally deposits the active film. While polymer crystallization can be characterized by grazing incidence small and wide angle x-ray scattering technique, the morphology detail, produced by this two-step film deposition process (the first step is the crystallization of low band gap polymers in a poor solvent due to evaporation of good solvent and a second step is the evaporation of additives, producing the final BHJ film), requires more effort to understand. Using two low band gap polymers, blended with modified fullerene derivatives, we investigated the morphological details produced by this additive driven morphology evolution real-time GISAXS and GIWAXD and complemented these studies with resonance soft x-ray scattering, high resolution TEM and scanning force microscopy methods. We observed that a multi-length scale morphology or hierarchical morphology exists in the final BHJ film, which gives good performance in solar cell devices.
Characterization Of Polyelectrolytes In Dilute Solutions: Light Scattering And Electrophysiology

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Abstract

Determination of molar mass and radius of gyration of polyelectrolyte molecules in dilute solutions at lower added salt concentrations from light scattering measurements continues to be a challenge. As an example, the measured molar mass in salt-free solutions by using the Zimm plot can be an order of magnitude smaller than the true molar mass. We have developed a new theory of light scattering from dilute solutions of polyelectrolytes as a function of added salt concentration. In terms of this development, we will present a method of analysis of light scattering to correctly characterize dilute polyelectrolyte solutions. We will also discuss the single-molecule-electrophysiology method whereby single polyelectrolyte chains are threaded through single protein pores embedded in membranes under an externally imposed electric field, and the accompanying modulations in the ionic current are measured. This technique allows the measurement of macromolecular length. We show how different molecular weight fractions of polyelectrolytes in aqueous solutions can be characterized.
Quantifying Protein Interactions From "Low" To "High" Concentrations Using Complementary Scattering Techniques

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Abstract

Interactions between proteins in concentrated solutions are of increasing interest, as many applications require proteins to be processed and/or formulated at high concentrations (~ 0.1 wt %) that cause issues with solubility, high viscosity, and/or aggregation. While traditional measurements of protein interactions in dilute solution (e.g., second osmotic virial coefficients, B22) have been used as surrogates in the past, it remains an open question as to how well dilute-solution measures of protein-protein interactions correlate or predict behavior at high concentrations. A generalized statistical mechanical Rayleigh scattering model allows one to quantify such interactions in terms of the protein-protein Kirkwood-Buff integral (G22), so as to overcome traditional dilute-solution limitations of the analysis of static laser scattering (SLS) data. This in principle can also be applied to q-dependent experiments such as small-angle x-ray or neutron scattering (SANS), as well as dynamic light scattering (DLS). Application of the theory to experimental LS, DLS, and SANS data is illustrated with two model proteins as a function of protein concentration (c) and NaCl concentration. The results highlight shortcomings of currently used models for c-dependent light scattering that cannot quantitatively describe the scattering behavior under conditions of strongly repulsive or strongly attractive interactions beyond the dilute regime. The theory also places bounds on where the canonical dilute-regime analysis is valid, based on the product of G22 and concentration. The analysis is also applicable to reasonably monodisperse nano-particle suspensions other than proteins.
Ensuring Accurate Size And Counts Of Protein Aggregates With Models And Reference Materials

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Abstract

One degradation pathway for protein-based drugs is the growth of protein aggregates or particles. Both industry and the FDA seek to accurately count and characterize these particles to assure the quality, efficacy, and safety of protein-based biopharmaceuticals. Two common methods for counting particles at effective diameters of > 1 µm are based on light scattering (light obscuration counters) and dynamic optical imaging (flow microscopes). These instruments rely on polystyrene latex (PSL) beads as calibration standards, but the properties of PSL beads differ greatly from those of typical protein particles. Protein particles are highly hydrated, with a correspondingly low refractive index, and are highly irregular in morphology. As a consequence, particle counts between light obscuration and flow microscopy may differ by a factor of 10 or more. To understand and correct for instrument errors requires a three-step approach:

• developing appropriate models for the instrument response,
• identifying and characterizing the physical properties of protein particles relevant to the counting method considered, and
• developing appropriate reference standards.

This talk will describe an instrument model for light obscuration and the development of reference standards. A light obscuration counter transforms light scattering of a particle into an apparent diameter. However, the scattering efficiency depends on the refractive index of the particle and the detection configuration. Applying this model effectively removes much of the discrepancy between light obscuration and flow microscopy measurements. In the area of reference materials, we are developing two types of polymer particles that mimic the optical properties of actual protein particles. In the first approach, ethylene-tetrafluoroethylene (ETF) is abraded to form a suspension of particles, covering the range 1 µm to 30 µm in effective diameter. ETF has several desirable properties: it is chemically inert and very rugged, and has a refractive index (1.40) very close to that of amorphous protein adsorbed on surfaces. When abraded from a solid block, the morphology of the resulting particles closely mimics that of typical protein particles (see figure). As an alternative method, we are also fabricating monodisperse particles using lithographic techniques. For our initial efforts, we have designed a wide variety of shapes using the epoxy-based photoresist (SU-8). We have produced particles as large as 300 µm and as small as 40 µm long rods with a 2 µm x 2 µm square cross section. A challenge for the lithographic approach is identifying a polymer with low refractive index that is of sufficient strength and stability. These candidate reference materials will provide a means of quantifying the instrument response for particles of both low optical contrast and irregular morphology.
Comparison of a candidate reference material (abraded ETFE) with protein particles formed from agitated human serum albumin (HSA).
High Resolution Characterization Of Proteins In Amorphous Solid Powders

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Abstract

Protein drugs are the fastest growing sector of the pharmaceutical industry. These large, complex molecules are subject to a variety of chemical and physical degradation processes. Arguably, the most serious type of degradation is aggregation, since the presence of aggregates is associated with changes in drug potency, which can be either greater or less than in the aggregate-free form. Aggregates are also associated with an increased potential for adverse immune responses in patients, which can be life-threatening.

In an attempt to preserve the native form and prevent aggregation, many protein drugs are marketed as solid amorphous powders, usually produced by lyophilization (i.e., freeze-drying) or spray drying. Of the nine protein drug products approved by the U.S. Food and Drug Administration (FDA) in 2011, five are solids. Currently, protein conformation in solid powders is characterized using vibrational spectroscopy methods (e.g., FTIR, Raman). At best, these methods provide semi-quantitative measures of protein secondary structure at the intact protein level, but lack sufficient resolution to allow the solid environment around aggregation-prone or labile sites to be defined and controlled.

To address the lack of high resolution methods for proteins in the solid state, we are developing solid-state hydrogen deuterium exchange (ssHDX) and solid-state photolytic labeling (ssPLL) to characterize protein conformation in amorphous solid powders. By using proteolytic digestion and mass spectrometric analysis (“bottom-up”), peptide-resolution can be achieved. This presentation summarizes our recent progress in developing these methods.
Advanced Hydrogels: Design And Characterization

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Abstract

Gels – polymeric networks swollen with a substantial amount of solvent – represent a fascinating class of soft materials, with wide-ranging applications in fields as diverse as biomedicine, pharmaceutics, personal care products, foods, sensors, actuators, flexible electronics, oil recovery, and adhesives. Physical gels are held together by non-covalent interactions, which may be as specific as hydrogen bonds, or as general as solvophobic association of insoluble blocks. Among the attractive features of physical gels are reversibility, stimuli-responsiveness, and tunability of macroscopic properties. There are exciting opportunities to design new gel systems based on block copolymers, given the relative ease with which tailored architectures can be synthesized by modern controlled polymerization techniques.

In this talk two classes of physical gels will be highlighted. In one, the ability of ABC block terpolymers to form novel gel structures in water will be demonstrated, where blocks A and C are mutually immiscible and hydrophobic, while B is hydrophilic. In particular, the formation of hydrogels by sequential association (first A, then C) leads to a remarkably sharp gelation transition, at a relatively low polymer concentration. In the second system, gels formed by hydrogen bonding between the endblocks of a fully soluble ABA triblock and a separate, C homopolymer “crosslinker”, will be described. In this case the solvating medium is an ionic liquid, which affords access to a wide range of temperature and unprecedented rheological response.
Application Of MALDI-TOF MS And IMS-MS For Elucidating Macromolecular Architecture

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Abstract

Recent advances in the field of matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-ToF MS) enable the determination of the exact molecular weight of polymers with sufficient accuracy as to provide invaluable data for determining molecular architecture. For example, initial work in the field of cyclic polymers suffered from the difficulty of proving whether a macromolecule exhibits a cyclic topology, however accurate molecular weight determination via MALDI-ToF MS, along with GPC chromatograms, can provide firm evidence for a range of different architectures. More recent instrument advances, such as the development of ion mobility spectrometry (IMS), offer an additional and valuable tool for confirming macromolecular architecture. Because IMS enables a direct correlation between the size of macromolecular ion complexes, and their molecular weight, powerful information about architecture and gas-phase conformation can be revealed. These tools compliment more traditional characterization methods for elucidating the structure of linear, branched, cyclic, star and other polymer architectures.
Inverting Models Of Polymer Rheology For Analysis And Characterization

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Abstract

Tube-based models of polymer dynamics have come a long way; however, the goal of quantitative prediction of rheology given structural information has remained elusive. Consequently, it would seem that any attempt at "analytical rheology", which seeks to use rheological measurements on an unknown polymeric sample to infer structural information by inverting tube-based models, is doomed. Fortunately, recent meta-modeling work using a Bayesian framework paints a surprisingly optimistic picture; its promise hinges on the extreme sensitivity of rheology to structural features such as long-chain branching. The success of this framework in characterizing the structure of "synthetic" star-linear blends, and metallocene-catalyzed polymers, suggests ways in which other heterogeneous sources of information about an unknown sample, such as the underlying polymerization kinetics, and size-exclusion chromatography data may be seamless integrated into the prediction engine. It opens up a slew of new opportunities and challenges.
The Structural Rheology Of Long Chain Branched Polymers - Measuring And Modelling Macromolecules In Flow

Tom Mcleish

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Abstract

"The Structural Rheology of Long Chain Branched Polymers - Measuring and Modelling Macromolecules in Flow"
Tom McLeish
Durham University

The fluid form of the polymers while they are being processed is remarkable scientifically and industrially important. The underlying physics shows a large degree of universality, connecting fundamental questions of polymer dynamics to industrial materials design. A global partnership of physicists, mathematicians, chemists and engineers is now beginning to unravel the tangled tale of polymer melts. Polymer physicists examine very well-controlled “molecular architectures” of polymers. Alongside the experiments, a powerful theoretical idea is employed by the theoreticians: each chain moves as if it were confined to a tube. The tubes allow only snaking motions of the chains they contain along their lengths. Mathematical versions of these pictures give predictions for the elastic memory of star polymers in astonishing agreement with experiment. Generalising to more complex architectures makes surprising predictions in non-linear response. Very recently this programme has been combined with numerical models of industrial polymerisation kinetics to yield predictive strain-hardening process rheology for LDPE and metallocene LCB resins. (1)

The polymer physics connecting branching structure to rheology also opens up a range of analytical tools supplying “windows” onto these structures, when interpreted in the light of modelling tools.

Contributed Lecture Abstracts
Different Approaches For The Hyphenation Of Size Exclusion Chromatography To Mass Spectrometry For The Structural Elucidation Of (Co-)Polymers

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Abstract

Size exclusion chromatography (GPC) is a widely used technique to obtain molar mass and molar mass distribution of a polymer. Whereas the data of non-polar homopolymers can be calibrated with commercially available standards (e.g. polystyrene, PMMA, PEG) or, if they have a high enough molar mass, can be determined directly with light scattering, the task is not that easy for copolymers and resins with low molar masses. Mass spectrometry on the other hand is a widely used detector in liquid chromatography and a powerful tool in polymer characterization – so why not use it in combination with SEC?

We have tested three different approaches for the hyphenation of SEC to MS, each of those having advantages and disadvantages, absolute “no go”s and ideal operating conditions. In this paper we present a comparison of the methods and how they can help to investigate the structure of novel copolymers:

1. Direct SEC/ESI-MS hyphenation: The solvents usually used in SEC are not compatible to mass spectrometry and the commercial HPLC-MS hyphenations can therefore not be used. By changing or mixing the solvent after SEC separation a system could be established which gives optimal results on an ESI mass spectrometer.

2. Fractionated SEC/MALDI-ToF MS: in this approach a sample is fractionated by SEC, usually collecting fractions of multiple runs, and then the polymer fraction is analyzed by MALDI-ToF MS using a conventional dried droplet technique (see Fig. 1).

3. Online SEC/MALDI-ToF MS: in order to overcome the tedious work of collecting fractions and preparing each spot by a dried droplet technique, it is advantageous to have an online MALDI sample preparation after SEC. This can best be accomplished by adding a matrix solution to the SEC flow after separation and processing this mixture through an ESI source mounted to a moving MALDI target.

In conclusion it can be said that mass spectrometry readily enhances the capabilities of SEC and gives a close insight into the separation behavior of complex polymers. Its value can even be enhanced if mass spectrometers are used that can perform MS/MS experiments – in this case even a structural characterization of complex molecules is possible (e.g. end group determination).
Fig. 1. SEC chromatogram of a vinylmelamine-styrene-copolymer, and the MALDI-TOF mass spectrum obtained from a low molar mass fraction showing different distributions.
Advances In Applications Of Polymer Characterization

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Abstract

Gel Permeation Chromatography (GPC), originally commercialized by Waters Corporation in 1963, is an important tool for the characterization of polymers. Incremental improvements have been made in the column technology and the system components since its introduction. However, significant advances have been minimal due to system and particle technology limitations. Typical GPC column packing materials are crosslinked styrene-divinyl benzene gels used with organic mobile phases, and hydrophilic methacrylate gels used for aqueous polymer analysis. The shortcoming of gel-based packing materials is their limited mechanical stability; hence must be used at relatively low backpressures. In addition, mobile phase switching capability is limited due to the swelling and shrinking of particles in different solvents, potentially resulting in loss of efficiency and irreproducibility.

Here, we demonstrate the advancements in chromatographic technology for polymer characterization, reducing the analysis times without sacrificing performance. The separation of various polymer samples including those with broad molecular weight distribution are shown. Advances in column technology facilitate the switching of mobile phases between different organic solvents, such as tetrahydrofuran (THF), toluene, and N,N-dimethylformamide (DMF), a less common practice using conventional GPC. Recent innovations in instrument and column technology provide a significant technological impact in the field of polymer science. Those improvements are speed of analysis, oligomer resolution, and the solvent switching capability.
Characterization Of Functional Poly(Ethylene Oxide)S And Their Corresponding Polystyrene Block Copolymers By Liquid Chromatography Under Critical Conditions In Organic Solvents

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Abstract

Poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) is a hydrophilic polymer which is ubiquitous in numerous biomedical applications owning to its good biocompatibility, such as the lack of toxicity and immunogenicity, non-biodegradability, and ease of excretion from living organisms. Besides its biological properties, the interest of PEO is related to the fact that the polyether backbone is fairly inert to most chemical reactions and soluble in a wide range of organic solvents. In addition, usually PEO has precisely defined terminal functionality, mainly primary hydroxyl group, which offers the possibility to perform further convenient chemical transformation to enhance and/or tune its chemical reactivity for different applications. These favorable biological and chemical properties, as well as the development of the living/controlled radical polymerization (CLRP) techniques, have stimulated an unprecedented research activity focused on both the chemical derivatization of PEO and the synthesis of PEO-based amphiphilic block copolymers. Whatever the applications in which PEO materials are used, their performance and properties are strongly influenced by the distribution of the molar mass, the yield of functionality, the chemical composition, the architecture, or the contamination by residual homopolymers.

Consequently, the quantitative functionalization of PEO and the quality of control are essential in order to obtain precisely defined PEO materials. Moreover, in order to build accurate composition/architecture/properties relationships, a complete and precise characterization of PEO-based materials obtained at different stages of the synthesis process is highly desired. In this context, one of the most powerful methods allowing for the separation of either different polymers bearing various functional end-groups (telechelic polymers) or block copolymers according to block length is liquid chromatography at critical conditions (LCCC). This chromatographic mode, halfway between size exclusion chromatography (SEC) and interactive liquid chromatography, consists of compensating the entropic and enthalpic interactions which govern the elution of the polymer chain. In these conditions, the polymer chain eluted at the critical conditions becomes chromatographically “invisible”, and the elution is independent of the molar mass.

Therefore this chromatographic technique was used to achieve the separation of functional PEO and PEO block copolymers. The optimum eluent is a mixture of 58.05% chloroform, 6.45% methanol, and 35.50% n-heptane (v/v/v) using a reverse phase (C8) column. Unlike what was expected, the elution mechanism is governed by the interaction of a polar endgroup with the column. In these conditions, poly(ethylene oxide) (PEO) functionalized with either an acrylate or alkoxyamine moieties were separated. This allows us to investigate the efficiency of the synthesis of poly(ethylene oxide)-b-polystyrene (PEO-b-PS) and polystyrene-b-poly(ethylene oxide) b-polystyrene (PS-b-PEO-b-PS) block copolymers prepared via the combination of 1,2 radical intermolecular addition followed by the nitroxide-mediated polymerization NMP of styrene. Amphiphilic diblock PEO-b-PS and triblock PS-b-PEO-b-PS copolymers were also separated from PEO homopolymers using the same experimental conditions. We showed that the PEO block is then invisible, and the calibration curve obtained using PS homopolymer standards could be used to determine the whole molar mass of the PS block in block copolymers with PS and PEO segments, with a weak influence of the architecture.
Block Copolymers of PS and POE

Elution Volume

CHCl₃/MeOH/n-Heptane
58.05/6.45/35.5

Functionality

Log M

Ve (mL)
Determination Of Polymer Composition And Composition Distribution By Thermal Field-Flow Fractionation

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Abstract

Thermal field-flow fractionation (ThFFF) is a technique that separates polymers according to their molecular weight and composition. The separation mechanism is based on polymer migration in the presence of a thermal gradient. In addition to the normal diffusion coefficient D, polymer motion is also regulated by the thermal diffusion coefficient DT. The DT/D ratio determines the equilibrium position of each sample component in the parabolic flow profile of the ThFFF channel. Components with a higher D and/or smaller DT will occupy the higher flow velocity streamlines and elute first. The retention time $t_r$ in ThFFF is

$$t_r = t_0 \frac{D_T \Delta T}{6D}$$

where $t_0$ is the channel void time and $\Delta T$ is temperature difference between the hot and cold walls. Thermal diffusion is a highly intriguing phenomenon and to date, no single theory is capable of explaining all observed phenomena. Nevertheless, existing experimental results and theories have enabled us to develop ThFFF as a method for determining composition and composition distributions of complex polymers. We and others have shown that DT is related to (co)polymer composition and average compositions can be readily obtained. However, if DT can be determined on-line for polymers eluting from the ThFFF channel, composition distributions are then possible. We accomplish this by using an on-line quasielastic light scattering detector to determine D (and hence DT) values as a function of $t_r$ (see Eq 1). The addition of a multangle light scattering detector allows the measurement of molar mass as a function of $t_r$ and hence provides an additional level of information.

This presentation will focus on the development of a ThFFF method and its use with multiple detectors to determine copolymer and terpolymer composition and molecular weight distributions. Polystyrene-polyacrylate polymers will be used to illustrate the distinct capabilities of ThFFF and highlight its benefits compared to traditional polymer characterization methods.

References

Ultra High Performance Size Exclusion Chromatography Of Synthetic Polymers

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Abstract

Size Exclusion Chromatography (SEC) is the preferred method for the determination of the molecular weight parameters of synthetic polymers as a result of its universality, reliability, reproducibility and low sample consumption. To achieve sufficient resolution of separated species, the column sets are composed of at least two, and more often, three analytical columns (300 x 7.5-10 mm ID). Typical flow rates are 1 - 2 mL/min in order not to damage the column packing by exceeding its back pressure limit. Therefore, resulting SEC separation run times are often in range of 30 to 60 min.

Substantial acceleration of SEC separations remains difficult to achieve due to column packing pressure limitations. Short and wide diameter SEC columns (50 x 25 mm ID) that allow high eluent flow rates (typically 5 to 10 mL/min) while still running at moderate backpressure are the only present solution to speed up SEC separations. A limitation to this approach is lower column resolution.

Ultra high performance size exclusion chromatography (UHP SEC) is a newly developed disruptive technology allowing separation of synthetic polymers with very short analysis times and improved resolution. Using a Waters ACQUITY® UPLC® system and BEH SEC columns packed with 1.7 µm particles, and a range of different pore sizes, UHP SEC separations of narrow commercially available standards are achieved within 2 minutes.
Size-Exclusion Chromatography Of Ultrahigh Molecular Weight Cellulose Ethers For Accurate Molecular Weight Distribution Characterization

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Abstract

Aqueous size-exclusion chromatography (SEC) coupled with multi-angle laser light scattering (MALLS) and differential refractive index (DRI) detectors was employed for determination of molecular weight distributions (MWD) of water-soluble cellulose ethers (CE), including both methylcellulose and hydroxypropyl methylcellulose. The weight-average molecular weights (Mw) of the studied cellulose ethers varied from 20 to more than 1,000 kg/mol, and the viscosities of 2 wt% solutions varied from 3 to 250,000 centipoise. Previous work employing right angle laser light scattering and differential viscometer detectors provided accurate molecular weight up to ~ 300 kg/mol. The main advantage of using MALLS is that it provides accurate molecular weights across the entire range of cellulose ether molecular weights. Flow rate and sample concentration were discovered to be critical SEC conditions for accurate MWD characterization of ultrahigh molecular weight cellulose ethers. A non-ideal SEC separation on cellulose ethers with Mw > 800 kg/mol was manifested by upward divergence of log Mw versus elution volume at larger elution volume at normal SEC flow rate such as 1.0 mL/min. As such, the determined number-average molecular weight (Mn) was erroneously large and polydispersity (Mw/Mn) was erroneously small. This non-ideality results from the late elution of high molecular weight chains. Non-ideal SEC elution was discovered to be eliminated by selecting sufficiently low flow rate and sample concentration. Thus, using carefully selected experimental conditions, SEC coupled with MALLS and DRI can provide accurate MWD characterization of higher molecular weight cellulose ethers covering the entire ranges of compositions and molecular weights of commercial interest.


Figure 1. Dependencies of the light scattering intensity I (90°, solid-line curve), refractive index RI (dashed-line curve), and weight-average molecular weight Mw (discrete points) on the elution volume for molecular weight standard CE4 1(red) and ultrahigh molecular weight CE4 2 at selected flow rate 0.2 (blue) or 1 (black) mL/min.
SEC-IR Coupled Technique To Characterize Polymer Grafting And Polymer Degradation

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Abstract

Infrared spectroscopy is the premier analytical tool for determining the composition and structure of polymers. The coupling of IR spectroscopy with size exclusion chromatography (SEC) through an automated solvent-removing interface provides a map of changing composition across the molecular weight distributions. The time-ordered IR spectra can be used to understand and monitor polymer modifications such as grafting reactions and to characterize the mechanism of polymer degradation.

The coupled SEC-IR system was used to characterize a polymer grafting reaction of poly(vinyl alcohol-co-vinyl acetate) copolymer (A) with an epoxy-terminated siloxane oligomer (B) under a specific catalyst condition. The reacted mixture can be mapped out by the A-specific IR band at 1739 cm$^{-1}$ and the B-specific IR band at 803 cm$^{-1}$ for the unreacted starting materials and the grafted product C. The band chromatogram based on B-specific 803 cm$^{-1}$ band gave a new polymer peak in the higher MW region than polymer A, confirming that silicone B was grafted onto the polymer A chain. The IR spectra of the grafted product C in this high MW region have all the IR features of both starting materials A and B. The ratio chromatogram of IR bands 803 cm$^{-1}$/1739 cm$^{-1}$ gave the grafting levels (i.e. how many B’s are attached to the polymer A chain) in the high MW region.

SEC-IR was also used to study the degradation behavior of a polymeric additive X (hydrogenated styrene-butadiene copolymer) used in a motor oil formulation under an accelerated ageing test (170°C, sampled every 12 hours). The high MW polymeric additive eluted first before its oligmeric degradants which eluted out before the low MW base oil which was then diverted away from the IR detector. With the ageing times increasing, more and more polymer X broke down to low MW degradants Z with broad MWD via oxidative cleavage as evidenced by the increased oxygen functional groups in Z’s: ether (1000-1200 cm$^{-1}$), oxirane (806 cm$^{-1}$) and carbonyl (1700-1750 cm$^{-1}$, 36-48 hr ageing). The remainder of polymeric additive X was partially oxidized as evidenced by the oxygen incorporation in the ether region (1000-1200 cm$^{-1}$) and into the oxirane ring (806 cm$^{-1}$), and appeared at the similar SEC elution time without any polymer chain breakdown.

Modified cellulose HPMCAS and Eudragit L100-55 (acrylate-acrylic acid copolymer) are commonly used in hot melt extrusion to make solid dispersions for low solubility drugs to improve their bioavailability. At high processing temperature over 200°C, SEC-IR detected succinic acid degradant and more hydroxyl formation along polymer chains of the HPMCAS excipient, which are important evidence to understand the degradation mechanism. At high processing temperature over 160°C Eudragit L100-55 excipient cross-linked to form a new functional group carboxylic anhydride which was detected by SEC-IR at 1805 cm$^{-1}$. Both cases will be presented to understand the polymer degradation mechanism under the thermal processing conditions.

SEC-IR is a useful tool to characterize polymer compositional changes such as intended polymer modification (e.g. grafting reaction) and unintended polymer degradation from thermal processing or ageing conditions.
Advances In SEC Analysis For Polymer Engineering Applications

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Abstract

This year marks the 50th anniversary of the first commercial Size Exclusion Chromatography (SEC) system or as it is commonly referred, Gel Permeation Chromatography (GPC). Since James Waters introduced the Waters GPC 100 system and associated Styragel® column offerings, significant advances have been made in polymer science and polymer molecular weight characterization based on that system.

Over the first decades many refinements have been introduced on the original concept. With the introduction of improved separation capacity, stable solvent delivery systems, automated sample introduction and robust detector technology, GPC has become an analytical work horse for polymer research and quality control laboratories. However, in the past two decades, little improvement has been made in basic SEC analytical systems to enable direct in-process analysis of polymerization reactions.

Recent focus on reduced solvent consumption and rapid through-put testing have proven useful, but with a tradeoff between analytical performance (resolution and sensitivity) and speed of analysis. Further, the dispersion and high dead volume of conventional refractive index detectors have limited the technological development required to break the speed vs. performance trade off for high quality rapid polymer analysis.

This paper reveals the limitations of current SEC technology and the obstacles that must be understood and addressed to advance to the next step in polymer molecular weight characterization. Further, this paper illustrates the promise of advanced SEC analysis based on a balanced approach of complete system design that enables direct real time process control of polymerization reactions. The examples provided in this study highlight the potential of rapid SEC analysis with high quality data generation for synthetic process optimization and polymer product confirmation.
SEC-IR Hyphenated System For Characterizing Chemical Compositions Of Copolymers And Polymer Mixtures

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Abstract

Mid-infrared spectroscopy is a well-established analytical technique to characterize the chemical composition of polymers. Hyphenating size exclusion chromatography (SEC) with an FTIR detector through an automated solvent-removing interface allows compositional and structural characterization across the whole molecular weight distribution (MWD) of a copolymer or complex polymer mixture. The SEC-IR system removes the solvent and deposits the chromatographic eluents as a continuous track on an IR-transparent ZnSe disc. The built-in interferometer simultaneously captures a set of time-ordered transmission IR spectra from the solid-phase deposit. The software system controls the data collection and performs data processing e.g. visualizing IR spectra across each SEC peak and plotting IR band chromatograms related to polymer functional groups. The ratios of those IR band chromatograms can be used to calculate copolymer compositional drift across MWD. The snapshot IR spectra at each elution time may be used for an IR database search to identify the chemical compositions.

The SEC-IR system is compatible with all common chromatography solvents such as water, acetonitrile, methanol, THF, DMF, DMSO, HFIP, o-DCB and TCB. Like LC–MS, SEC–IR is limited to the use of volatile buffers. Unlike MS which looks at molecular fragments, IR looks at the vibrational resonances of molecular bonds. For large molecules such as copolymers, IR's ensemble-averaging of like bonds simplifies data interpretation. This makes SEC–IR a useful tool to determine copolymer compositional variations across the MWD. For a complex polymer mixture each component can be identified through an IR library match, or monitored for any compositional changes during a polymer modification reaction or degradation from a thermal processing or ageing study.

(1) Analyzing Copolymer Compositional Drift: Copolymer compositional drift is a variation of the relative amounts of comonomers incorporated into the growing polymer chains during polymerization and is caused by monomer reactivity differences and/or monomer concentration variations in the reaction environment. The synthesis process must incorporate controls to either reduce composition drift, or to tailor it to a profile that yields desired end-use properties. Traditional techniques to analyze the composition drift are time-consuming and include preparative SEC, fraction collection and multiple sample preparations. SEC-IR provides a fast and single lab procedure in < 30 minutes to determine the composition drift. The author will discuss various compositional drift patterns from a set of styrene-butadiene copolymer samples analyzed by SEC-IR.

(2) Deformulation of Complex Polymer Mixtures: Deformulation of a flexible conductive ink obtained from the semiconductor industry completely identified its polymer (polyester and polyurethane) and additive (a latent cross-linking agent) components including their supplier information. This case study will be discussed in detail to illustrate the SEC-IR capabilities to deformulate complex polymer mixtures for competitive analysis, IP protection and analytical trouble-shooting in polymer-related industries.

(3) Characterizing Polymer Degradation: SEC-IR was also used to study the two different degradation pathways of a polymeric additive (hydrogenated styrene-butadiene copolymer) used in a motor oil formulation under an accelerated ageing test at 170°C. The high MW polymer additive eluted before its oligomeric degradants followed by the low MW base oil. With the ageing times increasing, more and more polymer additive broke down to low MW degradants via oxidative cleavage as evidenced by increased ether (1000-1200 cm-1), oxirane (806 cm-1) and carbonyl (1700-1750 cm-1) functional groups in the degradants. The remaining polymeric additive was partially oxidized with the oxygen incorporation showing in the ether and oxirane regions, but avoided polymer chain cleavage as evidenced by a similar SEC elution time.
Advances In Polymer Characterization Using Multi-Detector GPC And Light Scattering

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Abstract

Gel-permeation chromatography (GPC) is the most widely used tool for the measurement of molecular weight and molecular weight distribution of polymers. Historically, the elution volume of an unknown sample was compared with that of known standards to estimate molecular weight and distribution. However, so-called ‘conventional calibration’ is limited by the structural differences between standards and samples meaning that the measured molecular weight is only a relative value if the standards and samples are different polymers.

Static light scattering detectors measure the intensity of light scattered by the sample as it elutes from the column. Since the intensity of the scattered light is proportional to the sample’s molecular weight and concentration, they allow the direct measurement of the sample molecular weight independent of its elution volume. Furthermore, the angular dependence of the scattered light is also related to the radius of gyration of the molecule which can also be measured concurrently using a light scattering detector. An intrinsic viscosity detector can also be used as part of a GPC system to measure the parameter of intrinsic viscosity which can be combined with molecular weight data to calculate hydrodynamic radius. In combination these data allow detailed structural information of a polymer to be generated in a single GPC measurement which can be compared with other samples in Mark-Houwink or Conformation plots.

This paper will present data which shows that accurate information about polymer structure, branching, molecular weight and intrinsic viscosity can be obtained simply from a single GPC experiment. Furthermore, the extension of this technique to natural macromolecules such as proteins will also be demonstrated.
Equilibrium Kinetics In N-Alkane-PEO Micelles - A Time Resolved Sans Study

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Abstract

Block copolymers spontaneously self-organize into polymeric micelles when dispersed in a selective solvent, i.e. a solvent that is good for one block but poor for the other. Micellar growth is primarily driven by the incompatibility of the insoluble block with the solvent and counterbalanced by unfavorable configurations of the chains in core and corona of the micelles. An important prerequisite to reach and to attain equilibrium in micellar solutions is a continuous exchange of constituting chains. Although very important for fundamental understanding, experimental work on the equilibrium kinetics in block copolymer micelles is very rare in comparison with structural investigations. This is most likely due to the challenging problem to access chain exchange by suitable experimental techniques.

In recent years time- resolved small angle neutron scattering (TR-SANS) turned out to be a very successful method to investigate chain exchange kinetics of block copolymer micelles. The TR-SANS technique relies on a specific labeling scheme, the so-called kinetic zero average contrast (KZAC) technique, where deuterated and proteated micelles are mixed in a solvent that is contrast matched with the average of the oppositely labeled h and d polymers. When the chains exchange a measurable decay of SANS intensity is obtained due to the loss of contrast between micelles and solvent. This technique has led to an understanding of fundamental kinetic processes as described in more detail in a recent review [1].

In this contribution we will present new results on n-alkyl-PEO5 polymers (CnH2n+1-O-PEO, n=18, 21, 24, 27, 30) in aqueous solution. The n-alkyl-PEOs can be considered as hybrids between low-molecular weight surfactants and block copolymers. In our study it was found that the time scale for chain exchange extremely depends on the alkyl chain length, n, as a consequence of a double exponential dependence of n on the exchange rate, R(t). As expected from theory we observed a first order kinetic process which is characterized by a single exponential relaxation function, R(t) ~ exp(-t/τ). Both findings directly confirm that polydispersity of the core forming block leads to a pseudo-logarithmic time dependence, R(t) ~ ln(t), as previously found for real block copolymer systems [2,3]. Ideal conditions for real time measurements are obtained for the C27-PEO5 polymer. Here chain exchange is slow at room temperature but can be effectively accelerated by moderately increasing the temperature such that the full relaxation process can conveniently be followed within a time window of 30 min. Time temperature superposition reveals an Arrhenius type behavior where the characteristic times show a linear dependence for 1/T. The corresponding activation energy was determined to be 150 kJ/mol. Increasing the PEO chain length in this system reveals a slowing down of the rate but to a much lesser extent. According to the theory the PEO degree of polymerization comes in only as a prefactor to the activation energy term and thus influences the rate only in a single exponential fashion while the value of the activation energy stays constant. A summary of the main results will be presented and discussed in terms of the Halperin & Alexander theory [4] for the relaxation kinetics in block copolymer micellar systems.

Small-Angle X-Ray And Neutron Scattering Study Of A Protein-Cryoprotector System In Liquid, Supercooled Liquid, And Frozen States

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Abstract

Many protein drugs are either stored as frozen solutions, or converted into the solid state by freeze-drying, in order to improve the long-term stability. However, storage in the frozen or freeze-dried state does not guarantee long-term stability, and aggregation is often observed after freeze-thaw or reconstitution of freeze-dried powder. In this study, synchrotron wide-angle X-ray scattering, small-angle X-ray scattering, and small-angle neutron scattering have been used to investigate changes in a model protein-cryoprotector system under representative pharmaceutical processing conditions. To separate the effect of freeze-concentration from the impact of ice/solution interfaces, solutions with variable concentrations of the protein and a cryoprotector have been used in the temperature range of 298K to 100K. Composition of the freeze-concentrated solutions has been estimated from the synchrotron wide-angle scattering, in which formation of hexagonal and cubic ice has been monitored as a function of temperature and solute concentration. Analysis of the small-angle scattering data indicate that the structure factor of protein molecules in the freeze-concentrated solution in the presence of the ice phase may be different from that observed in a highly concentrated solution in the absence of ice. The study indicates that ice/solution interfaces probably play a major role in destabilization of protein molecules during freezing and freeze-drying.
Detection Of Polymer-Chain Branching In Complex Polymer Systems Including Linear Polymer Species

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Abstract

The role of size-exclusion chromatography (SEC) with multiple detection is to yield as much as possible information about the nature of the analysed polymer. This holds especially for branched polymers where the presence of the branched species is possible by a decrease in intrinsic viscosity compared with a polymer with the linear chain and (almost) the same chemical composition and therefore hydrodynamic properties of the linear chain. The decrease in intrinsic viscosity is caused by the volume contraction of molecules due to the branching. However, the interpretation of the experimental results and the estimation of the branching in terms of the number of the branch points per (randomly) branched molecule or number and length of grafts per grafted molecule depends on the model used for the interpretation of the results. Further complicating factors is the heterogeneity of the sample with respect to branching. The local dispersity is the direct consequence [1] in the most favourite case of random branching described by the classical theory [2-3] with the unimodal distribution of molecular weight/chain-lengths. In real branched polymers bi-or multimodal elution curves are frequently observed which suggests multimodal distribution of molecular weights with branching predominantly present in one of the portions of the distribution function. In such cases, the elution curves can be separated into parts treated separately [4].

References

[4] M. Netopilík et al., prepared for publication
Separation And Characterization Of Latex Particles By Asymmetric Flow Field Flow Fractionation And Dynamic Light Scattering

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Abstract

Poly(tetrafluoroethylene) latex particles have been analyzed and sorted according to size using asymmetric flow field flow fractionation (AF4) coupled to multiple-angle light scattering (MALS). Characterization of the fractions by regular and depolarized dynamic light scattering confirmed that small components of the particle distribution elute prior to large ones, as expected for field flow fractionation. The measured radii of gyration of the optically and geometrically anisotropic particles are consistent with sizes determined from transmission electron microscopy. The AF4/MALS method is an effective alternative to electron microscopy for characterization of colloidal particles. A certain amount of heterogeneity remains in the fractions, but their quality for use as diffusion probes is improved.
Application Of Local Thermal Analysis In The Field Of Polymer Science

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Abstract

A basic understanding of physical and chemical properties of polymers is of fundamental importance for the development of advanced polymers. Conventional methods reach their limits for applications such as thermal investigation of thin films, immiscible polymer blends, crystal structures, etc., since they only measure thermal bulk properties of polymers. Therefore, a method is proposed for thermal characterization of polymers in the nano-scale using scanning force microscopy (SFM) in combination with heatable cantilever probes. The SFM system engages the thermal probe with a constant force on the polymer surface and allows controlling the heat at the tip. During measurement the load force is maintained stable by a closed feedback loop holding the deflection signal constant while adjusting the displacement sensor (z-sensor). Due to thermal expansion of the sample during heating, the z-sensor signal starts to decrease in order to maintain a predetermined cantilever deflection. At the glass transition temperature the tip starts to penetrate the sample, since the viscosity of the polymer sample degreases significantly under the heated tip. Local thermal analysis (LTA) offers high spatial resolution (< 100 nm) making this method interesting for thermal investigations of polymer surfaces. Therefore, LTA is based on an appropriate temperature calibration, which provides a reliable correlation between the applied voltage and the temperature at the tip. As the presented technique is substantially more susceptible to environmental changes than comparable macroscopic methods, different parameters that influence the performance are evaluated such as heating rate, film thickness, and substrate temperature. In this study LTA is used to investigate the morphology of randomly distributed isotactic propylene-1-hexene-copolymer (PHCP) with a focus on local thermal properties. From the research that has been carried out, we can conclude that it is possible to investigate the differences in softening temperature of α- and β-structure of PHCP.

The basic experimental configuration for conventional local thermal analysis builds an electrical circuit consisting of a controlled voltage source, two equal reference resistances, and the cantilever resistance with a resistive area close to the tip. When a voltage is applied this area heats up, due to Joules heating.
Molecular Mobility In Polymers By Dynamic FT-IR Spectroscopy Using Continuous Scan Acquisition

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Abstract

Combination of Dynamical Mechanical Analysis with FT-IR spectroscopy allows studying dynamical behavior of polymers on molecular level. Step-scan FTIR technique used previously for this studies produces data with low signal-to-noise ratio even after several hours of acquisition time.

A new technique is proposed that allows recording of high quality FT-IR spectra of polymer film under the periodical stress within few minutes of acquisition time. Dual channel analog-to-digital converter is used for simultaneous recording of FTIR interferograms and periodical stress. Two 3D data arrays are generated after the several scans of the spectrometer: 1) Set of double modulated interferograms 2) Set of time-resolved stress. Software retrieves IR spectra that change in-phase and out-of-phase with the periodical stress and generates 2D-IR plot.

Application of this technique to study molecular mobility in polymers under the periodical mechanical stress will be discussed in details.
Nanoscale Dynamic Mechanical Spectroscopy Of Polymer Blends And Composites

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Abstract

Atomic Force Microscopy (AFM) has been a widely utilized tool in both industry and academia for imaging the surface of a material with nanoscale resolution. Today’s polymer blends and composites are more complex than ever, leading to challenges in characterizing the distribution of different components in the blend or composite. Lorentz Contact Resonance (LCR) allows for the clean excitation of the contact resonance modes of a Thermalever™ AFM cantilever. The contact resonant frequency and amplitude of these resonances are dependent on the stiffness of the material in contact with the probe. When tuned to a particular resonant frequency and scanned across a sample, the Thermalever™ probe can obtain a qualitative map of the varying stiffness of each component on the surface of a sample. Each individual component can then be highlighted by tuning to its resonant frequency and scanning the surface. This results in the visualization of the location and size of the domains of each component in a polymer blend or composite, greatly increasing our understanding of how these blends form. Furthermore, the Thermalever™ probes are fabricated with a resistive heating element at the end of the probe allowing for the controlled heating of the probe. Once a domain in a blend or composite has been identified using the LCR technique the Thermalever™ probe can then be placed on the region of interest and nanoscale thermal analysis (nanoTA) measurements such as glass or melt transition temperatures can be obtained. Measuring thermal transitions on highly filled or highly cross-linked materials can be challenging. However, the ability to track the contact frequency of a Thermalever™ probe, while simultaneously heating allows for the determination of thermal transitions on these challenging samples.
2D Chromatography And The Development Of Advanced Engineering Polymers

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Abstract

In the engineering polymer industry, product developers are facing a challenging environment with an insatiable demand for new materials. To achieve growth, the business seeks to increase its share in existing markets by improving the material's performance – a necessary response to the pressure from the competition and the demand from the customer. Another avenue for growth exists for the business by capturing new markets. In addition to these market driven pressures, the variation of raw material prices (i.e. monomer) forces sometimes product developers to re-invent well-established recipes in order to minimize manufacturing costs. Also, patent filing is becoming increasingly complex, with the Patent Office demanding intimate details about a polymer's structure in order to prove the novelty of a process or material.

In this paper we will discuss how two-dimensional chromatography (gradient polymer elution chromatography x gel permeation chromatography) is playing a growing role in supporting the product developers and process chemists. To illustrate this, the examples of several industrially relevant polymers will be examined. I will show how 2D data can give clues to the degradation mechanisms of a complex polymeric material after abusive processing or exposure to a harsh environment – therefore providing a solution to troubleshooting the formulation. In another example, I will show how the 2D data provides an insight into the process employed to manufacture a polymer, creating opportunities for improvement by establishing the structure/process and structure/property relationships.
Characterization Of Morphology And Orientation Of Uniaxially Oriented Cast Films Confocal And Polarized M-Raman Imaging-Spectroscopy

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Abstract

iPP ring-samples sheared by Pirouette-dilatometer showed that local variations in crystallinity and orientation can be investigated using polarized confocal µ-Raman microscopy. To investigate whether this method is suitable for a quantitative estimation of crystallinity and orientation of these sheared samples, materials with known orientation (measured via WAXS) were measured via confocal µ-Raman spectroscopy. The orientation was measured with polarized Raman spectroscopy, whereby the same area was scanned with different polarization.

The average and local crystallinity and the depolarization ratio of iPP Films (MDO and Cast) was estimated and compared to the WAXS measurements. The Hermans orientation function was as well estimated and found to be also in good correlation with the WAXS data.

By the means of these results a method was developed and applied for the characterization of the samples with undefined orientation prepared with the Pirouette dilatometer. It was found, for example, that the stretched sample shows a lower but more homogeneous crystallinity degree (on the surface), then the unstretched specimen (see image).

Crystallinity degree unstretched (a) and stretched (b) sample
Surface Analysis And Characterization Of Plasma-Treated Polypropylene (PP) And Polyamide (PA) Films By Contact Angle Measurements, Scanning Electron Microscopy (SEM) And Atomic Force Microscopy (AFM)

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Abstract

Polymers are used in a wide variety of applications including packaging and labeling, textiles, stationery, automotives, laboratory equipment, etc. A low surface energy may be desirable in them for several applications, but for other applications it is a disadvantage, which has to overcome. Polypropylene (PP) and polyamide (PA) are among the most widely used polymers in the industries. As the surface energy of PP and PA is also quite low, their surface properties such as hydrophilicity, adhesivity, printability, etc. do not often meet the requirement for industrial applications. In order to extend their application range, different methods have been developed to modify their surface properties. Among them, atmospheric pressure non-thermal plasma treatment is a convenient and environmentally friendly way to obtain these modifications by introducing new chemical groups at the surface without affecting the bulk properties. Among various atmospheric pressure non-thermal plasma sources, atmospheric pressure dielectric barrier discharge (APDBD) using line frequency (50 or 60 Hz) is attractive for industrial applications as it avoids the high costs associated with vacuum-based plasmas and overcomes the power supply heating deficiency of high frequency plasmas. Therefore, in this study, commercially available polypropylene (PP) and polyamide (PA) films (Goodfellow Ltd., UK) are treated in atmospheric pressure dielectric barrier discharge (APDBD) using line frequency (50 Hz) operating in air and argon. The surface properties of the plasma-treated PP and PA films are characterized using contact angle measurements, surface free energy calculations, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The polymer films show a remarkable increase in surface free energy after plasma treatment. SEM and AFM analyses of the plasma-treated polymer films show that plasma treatment introduces greater roughness on the polymer surface leading to the increased surface free energy.

SEM and AFM observations of plasma-treated polymer films
Investigating The Significance Of Submicron Particles For Protein Pharmaceutical Stability

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Abstract

Historically, the control of particles in injectable biopharmaceuticals has been based primarily on visual inspection for visible particulates and on particle counts for subvisible particulates larger than 10 and 25 microns using light obscuration. Over the past several years, concerns regarding the impact of subvisible particles on quality and safety have stimulated pursuit of more rigorous control methods as well as a better understanding of the origins and significance of such particles. A greater diversity of primary container closure configurations, materials, and devices has also heightened awareness of new incompatibilities potentially causing particles as contaminants and degradation products. Industry efforts to date have focused primarily on particles larger than 2 microns. In our laboratory we have investigated the significance of submicron-sized particles using nanoparticle tracking analysis and micro flow imaging. This presentation will describe recent studies to evaluate submicron particles in a prefilled syringe drug product in the presence and absence of silicone oil.
Surface Protein Adsorption Characterization By Quartz Crystal Microbalance With Dissipation (QCM-D): Case Studies

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Abstract

Quartz Crystal Microbalance with Dissipation (QCM-D) is a technology to measure the binding of a solute or suspended substance in solution to the surface of a test crystal which is periodically oscillated at high frequency by an alternating applied voltage. Any addition of mass to the crystal surface causes a proportional change in the frequency of oscillation of the crystal. Additionally, the visco-elastic properties of the adsorbed layer(s) can be inferred by monitoring the decay of oscillations and dissipation of energy into the layer – the higher the deformability of the layer, the stronger the dissipation and the faster the decay of oscillation. QCM-D technique has been used to monitor the difference in adsorption properties of “protein 1” to glass and stainless steel surfaces. Protein 1 in full formulation showed significant affinity to stainless steel coated crystal and none to a glass coated crystal which were pre-treated with placebo. Further, affinity of protein 1 to two types of filter surfaces was investigated. In buffer alone, protein adsorbs less on PVDF coated crystal than cellulose coated crystal at lower protein concentrations. Pre-treatment of the surfaces with placebo abolishes subsequent protein binding at relatively higher concentration to either surface in full formulation.
Use Of Simultaneous Multiple Sample Light Scattering (SMSLS) For Determination Of Equilibrium Properties And Aggregation Kinetics Of Protein

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Abstract

SMSLS permits high sensitivity, continuous monitoring of the stability of protein formulations for multiple, independent samples under different conditions, such as temperature, concentration, shear, and buffer composition. Monitoring can continue for weeks or months at a time without interruption and new samples can be introduced at any time. Here, two monoclonal antibodies (mAb) were studied, one of high stability and the other prone to aggregation. The aggregation rates of each mAb increased by six orders of magnitude over the temperature range 40°C to 80°C and were found to have similar activation energies under Arrhenius analysis. Nonetheless, the unstable mAb had aggregation rates 100 times faster at any temperature than the stable mAb. Under equilibrium conditions the molecular weight and virial coefficients of each mAb were determined by SMSLS and self-diffusion coefficient D by dynamic light scattering (DLS). SMSLS was measured for the stable mAb at concentrations up to 190mg/ml and the values of the second, third, and fourth virial coefficients A2, A3, and A4, respectively, were remarkably close to the suite predicted for a hard sphere whose hydrodynamic radius RH was equal to that obtained from D via the Stokes-Einstein relation (5.9nm). In contrast, A2 for the unstable mAb was 14 times smaller than that of the stable mAb and 22 times smaller than the hard sphere value from its RH (8.7nm). An hypothesis arising from this is that a hard sphere relationship among A2, A3, and A4, together with values in accord with RH may be a good predictor of protein stability.

Further analysis of protein aggregation kinetics showed that below about 40°C the mAb were dramatically less stable than would be predicted by extrapolation of the Arrhenius results above 40°C to lower temperatures. In fact, aggregation became completely stochastic below 40°C with no correlation among different temperatures. It is surmised that there are other stochastic variables at work at these lower temperatures that dominate the aggregation process. It is not known what these factors are, but they may involve sonic, convective, or shear perturbations, density fluctuations, exposure to certain surfaces, etc.

The early phase kinetics for both mAb are linear and very reproducible. A convenient representation is Mw/Mo vs time, where Mo is the mass of an unaggregated mAb and Mw the weight average mass of the entire population of aggregated and unaggregated protein at any time. At later stages of aggregation, i.e. at high Mw/Mo, the process becomes erratic and irreproducible. For these mAb as few as 3 dimers could be detected among 1,000 unaggregated proteins by the SMSLS instrument. The advantage of such sensitivity is that it allows very early detection of aggregation and accurate kinetic rate determination. Together with the multiple independent sample capability, early phase aggregation detection and quantification by SMSLS should accelerate the pace of protein formulation stability testing.
Aggregate And Particle Analysis For Protein Therapeutics – Current Methods, Challenges And New Trends

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Abstract

Aggregate and particle analysis remain an integral part of the development of biopharmaceutical products. This is amongst others important because of the potential risk for unwanted immunogenicity caused by aggregates and/or subvisible particles. Protein aggregates and particles differ in their properties, such as size (nm to mm), shape and conformation. Therefore, a wide range of methods is required for a comprehensive characterization of these impurities. In this context, emerging techniques gain importance especially for subvisible particle analysis to meet the rising expectations from the regulatory authorities to characterize subvisible particles in the submicron and micron size range. It is currently expected that the whole size range from submicron to micron particles should be covered by orthogonal approaches already starting in the early stages of development: micron particles larger than 1-2 µm should be quantified and identified, whereas submicron particles from 0.1 to 1 µm should be characterized as far as possible. Particle data should be linked to clinical results to allow a risk analysis of particles for the application of the product to the patient. Control strategies to minimize particle levels within the product should be developed based on processing, characterization and clinical data.

Within the talk an overview on methods for aggregate characterization (e.g. size exclusion chromatography, field flow fractionation) and particle analysis (e.g. light obscuration, flow imaging techniques, dynamic light scattering, nanoparticle tracking analysis and resonant mass measurements) is given. Examples will be given showing applications, benefits and limitations of these methods applied during the analysis of pharmaceutical protein products.

One example is the evaluation of flow imaging microscopy and resonant mass measurements for the differentiation of silicone oil droplets and protein particles. For this purpose a custom made data filter was developed to differentiate silicone oil and protein particles in flow imaging microscopy based on the properties of the generated images.

Another example will illustrate possible influence of formulation and protein particles, such as refractive index on light based techniques, e.g. light obscuration of flow imaging microscopy.
Protein Quaternary Structure Characterization: The Effect Of Protein Self-Association On Analytical Method Development

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Abstract

Size exclusion chromatography (SEC) is the method of choice for routine analysis of protein aggregates across the biopharmaceutical industry. SEC has also been used historically for native protein-protein association to gain insight about the protein quaternary structure and the thermodynamics and kinetics of the association. However, weak protein association may not be detected due to significant sample dilution and protein-column interaction. On the other hand, stronger association may also complicate the SEC method validation due to the changes as a function of sample loads. Orthogonal methods, such as analytical ultracentrifugation (AUC), should facilitate further characterization of the protein association at the concentration and buffer conditions that are difficult to implement in the SEC method. Implementation of orthogonal confirmation during SEC method development will help better understand the performance of the method and ensure its suitability for intended use. Several case studies are provided.
Synthesis Of Polyhydroxyalkanoates (PHA) From Pseudomonas Aeruginosa, Using Glucose As A Carbon Source. An Alternative To Mitigate The Environmental Impact From CTSA Approach

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Abstract

Companies need to generate and implement techniques for the production of synthetic materials (polymers), as an essential tool to meet basic requirements in modern societies. The production, consumption and indiscriminate use of these materials have generated considerable environmental impact by altering the normal course of the ecosystem. Also, the excessive use of these polymers has increased this problem, because they are difficult to degrade and long lasting. For this reason, man has been interested in finding solutions to mitigate the environmental impact. One of these is to generate materials that easily degrade in the environment as is the case of biopolymers (PHA), defined as intracellular polyesters synthesized by different bacterial species. These materials have characteristics similar to synthetic polymers but unlike the latter, the PHAs are degraded completely reducing the environmental impact. In this regard, the present research was based on the synthesis of PHA from Pseudomonas aeruginosa, using glucose as a carbon source. In turn, variables such as time, pH and concentration of glucose, which affect the growth of PHA, were studied.
Polypeptides From Inside Out: Techniques For Investigating Their Dynamical Behavior And Properties

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Abstract

All molecules, even macromolecules, are small entities. Delivering them where they are needed is a challenge. Polypeptides, molecules featuring properties such as chirality and ability to undergo to conformational changes under applied stimuli, can be delivered by coupling them to silica colloids, then cutting the polymer free. The large colloids and their polymer payload present extra characterization challenges. These will be discussed in the context of polymer conformation after delivering.

This work was supported by National Foundation Award 1005707 (DMR).
Study Of The Mechanism Associated With The Mucoadhesion Phenomena In Polymers For Pharmaceutical Applications

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Abstract

Mucoadhesive polymers have been used extensively in the pharmaceutical industry, to produce pharmaceutical dosage forms that could remain in contact with specific tissues for a long time. In order to induce bioadhesion, the polymer should have functional groups, such as carbonyl, thiol, or hydroxyl; that promote the interaction with the mucus, which is mainly composed by water (95%) and mucins (5%). Generally speaking, mucins may be considered as polymers with very high molecular weight and complex structures. Therefore, in order to understand the adhesion phenomena, it is necessary to study the interaction between the two polymers. In this regard, several approaches to measure the force of adhesion between a polymer, in the form of a film or a tablet, and the mucin, are presented in this contribution. Also, the specific interaction polymer/mucin via dilute solution viscometry, was studied. After analyzing the results, it was concluded that in order to elucidate the actual state of the polymer/mucin interaction, additional measurements were needed at smaller scales Molecular simulations provide an alternative to study such phenomena at very low scale e.g., molecular, allowing the study of the effect that several parameters, can have on the bioadhesive character of some polymers, under conditions that are not feasible in experimental research. In this work, Dissipative particle dynamics (DPD), a coarse-grained simulation technique successfully used in several polymeric systems, is used. In the DPD simulations, mucins were represented as series of coarse-grained beads forming different geometrical arrangements, resembling the different functional groups in the molecule. Mucin adsorption, desorption over a polymer layer, and the effect of shear were studied by DPD.

Finally, some insights about the relation between the molecular simulation and experimental results are also given. Financial support for this research was provided by COLCIENCIAS (grant number 110152128526), and by the Universidad Nacional de Colombia (research grant number 15371).
Left: Arrange of beads for a linear mucin with cysteine type beads in both chain ends, used to simulate polymer/mucin interaction. Right: Micrograph of the wall of a calf intestine after peeling a bioadhesive polymeric membrane.
Customized Triglycerides For Polymer Synthesis

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Abstract

There has been a lot of recent interest (1-3) in using vegetable oils as biodegradable and renewable raw materials for the syntheses of various biobased materials. Many polymers have been made from vegetable oils, particularly using reactions involving olefinic functionalities on the triglycerides. In many of these applications the amounts of oleic, linoleic, and linolenic functionalities in a vegetable oil have a major role in the reactivities of the oil, the speed of the reactions, and the nature of the polymer products. For example, linseed and tung oils have numerous olefinic bonds and are the preferred materials to use in drying oils (4,5). In superacid-catalyzed polymerization, it is known that oleic functionality alone cannot bring about polymerization; linoleic and linolenic functionalities are needed (6). In polymerizations involving ene reactions (7), higher levels of linoleic and linolenic functionalities are known to increase the rate of polymerization, and linolenic functionality produces more complex polymer structures.

Our approach is to customize the amounts of mono-ene and di-ene functionalities through hydrogenation. In this way, we have better control of the structure of the products and rate of the reaction. In this work a detailed hydrogenation study is carried out using commercially available Ni, Pt and Pd catalysts under different hydrogenation conditions. Kinetic modeling of the observed data has been done so that a detailed understanding is obtained of the hydrogenation process. With good knowledge of reaction kinetics, triglycerides with mono-ene content up to 60% or linoleic acid content up to 53% can be produced, and these functionalities can be derivatized to produce specific biobased products.

References:
GPC And NMR Characterization Of A Lytic Copolymer

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Abstract

Cationic polymers and copolymers are valuable as DNA-carriers and bactericides among other uses in Life Sciences. The study of how parameters as molecular weight, relative composition and polydispersity affect the efficiency of such materials for selected applications are still an open field in many cases. Balance of overall polarity, relative composition and total molecular weight can lead to very effective bactericide capacity as well as a better selectivity towards prokaryotic cells, for instance. In this work a poly(methyl methacrylate) - block - poly[2-(dimethylamino) ethyl methacrylate] (PMMA-b-PDMAEMA) has been characterized by a combination of GPC and 1H-NMR. Due to its positive charge below pH~9 PMMA-b-PDMAEMA has the ability to break biomimetic models such as vesicles of natural lipids in a similar way as some bactericide peptides do justifying the relevance of its complete and exact characterization.

Since copolymer molar mass standards are not available and Light Scattering determinations are very time-demanding for that kind of material, a combination of GPC and NMR was chosen to get the molar mass average and composition with the best accuracy possible, taking into account that the use of PMMA standards for copolymers gives a not accurate estimate of the average molar mass. Since in this case the block copolymers were made by RAFT in a two-step fashion, the first block, PMMA, had its molar mass determined exactly by classical GPC and the PDMAEMA/PMMA ratio of each copolymer was then measured by 1H-NMR. That is possible because there are protons in the blocks with different chemical shifts so that the peak area is a feasible way to compare the blocks length.

Results showed a marked difference between the molar mass obtained by classical GPC and the combination GPC-NMR. Table I presents the molar mass averages and composition for three different RAFT-synthesized PMMA-b-PDMAEMA planned to have different total molar and different block ratio. Plain GPC underestimates the size of the PDMAEMA block compared to GPC-NMR combination approach.

In conclusion, the GPC-NMR approach has been proved to be a simpler and much more accurate way to measure the total molecular weight as well as the composition of the particular system studied (PMMA-b-PDMAEMA). The method is indicated to be used with similar systems (new copolymers with variable block composition).

Table I: Number molar mass averages (Mn) measured by GPC and GPC-NMR combination.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mₙ by plain GPC (kg mol⁻¹)</th>
<th>Mₙ by NMR (kg mol⁻¹)</th>
<th>Mₙ by GPC-NMR (kg mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>PMMA-b-PDMAEMA</td>
<td>PDMAEMA</td>
<td>PMMA-b-PDMAEMA</td>
</tr>
<tr>
<td>I</td>
<td>4.98</td>
<td>28.4</td>
<td>33.4</td>
</tr>
<tr>
<td>II</td>
<td>4.83</td>
<td>1.46</td>
<td>6.29</td>
</tr>
<tr>
<td>III</td>
<td>9.37</td>
<td>3.48</td>
<td>12.8</td>
</tr>
</tbody>
</table>
pH-Responsive Amphiphilic Copolymers Via RAFT. Synthesis And Characterization

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Abstract

An area of considerable interest in polymer chemistry is the synthesis of amphiphilic macromolecules with precisely structured architectures. Synthesis of amphiphilic diblock and gradient copolymers of 2-(dimethylamino)ethyl (meth)acrylate with styrene via Reversible addition fragmentation chain transfer (RAFT) polymerization in N,N-dimethylformamide was followed in real time by the use of Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP). Combined light scattering, spectroscopic and conductivity measurements allowed conversion, copolymer mass, gradient composition, as well as the degree of reaction control and efficiency of the second block addition to be determined. Thus, controlling the composition and chain length during the synthesis, and the environmental conditions, post synthesis allowed properties of the copolymeric material to be influenced.

A comprehensive characterization of the behavior of the amphiphilic copolymers in both organic and aqueous media was made offline by additional techniques, each of them focused on different aspects in the copolymer behavior.

It is hoped that the combination of the different techniques involved in this study, both online and offline, offers the advantages of a complete way to control material properties at each step of the entire process, by design of the copolymer composition and chain length, optimization of the polymerization process via online monitoring, and by a thorough study and verification of the material properties, according to specific applications.
Interfacial Curvature Effects In The Self-Assembly And Responsiveness In Polypeptide-Based Star And Triblock Copolymers

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Abstract

This study involves the bottom-up design and tunability of responsive, amphiphilic peptide block copolymers. The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic diblock, triblock and star copolymers containing poly(lysine) (PK) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. These materials are shown to respond to pH, due in part to the helix-coil transition in the peptide chain, but also due to changes in curvature of the assembly at the interface. This talk will present some recent studies in solution morphology transitions that occur in these materials as a result of the helix-coil transition and associated charge-charge interactions. We exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH due to morphology transitions.
Countervailing Effects Of Ionic Strength And Composition On The Lower Critical Solution Temperature (LCST) Of Copolymers Of Poly(N-Isopropyl Acrylamide) And Acrylamide

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Abstract

Poly(N-isopropyl acrylamide) (pNIPAM) is a well-known stimuli-responsive polymer, with a Lower Critical Solution Temperature (LCST) of 32 °C. Acrylamide (Am) is a hydrophilic polymer, which readily copolymerizes with NIPAM. Past results have established that the presence of Am in a NIPAM-based copolymer raises the LCST.1 Other results have established that the addition of NaCl to the solution lowers the LCST of p(NIPAM) homopolymer.2 The first observation of the appearance of reversible LCST behavior during a copolymerization reaction of NIPAM/Am was made by combining Automatic Continuous Online Monitoring of Polymerization (ACOMP)3 with custom in-development second-generation ACOMP (SGA). A custom built Simultaneous Multiple Static Light Scattering (SMSLS)4 instrument was then used to measure the LCST of the resulting polymer of those reactions.

The results verify early work regarding the effects of composition and NaCl on the LCST’s of the copolymers. The salting-out effect of NaCl on the copolymers was measured, extending the idea from previous results on the homopolymer. Finally, the relative strengths of the composition and salting-out effects are compared and the interaction between the two effects is measured. There are compositions for which the composition effect totally overwhelms the salting-out effect, and that no amount of NaCl will cause an LCST below the boiling point of the solution.

Because of some difference in reactivity ratios between Am and NIPAM in the free radical synthetic reactions, there is some composition drift during the reaction. Because the composition effect on LCST is quite large, there is a measureable variation of LCST within the polymer population that stretches out the transition temperature. Analysis is underway to estimate the expected variation of composition within the polymer population. From that the fraction of chains in the population that undergo the LCST at a given temperature can be made. This can be correlated with the light scattering curves from the SMSLS.

Synthesis And Properties Of Biohybrid Glycopolymers And Chimeric Polysaccharides Capable Of Ionotropic Gelation

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Abstract

Alginate is a heteropolysaccharide extracted from brown algae. At a molecular level, it is a linear copolymer of (1?4)-linked ß-D-mannuronic acid and a-L-guluronic acid residues distributed in long homopolymeric blocks and in shorter alternating copolymer blocks. An attractive feature of alginate is the possibility to extract the constituting oligosaccharides by controlled hydrolysis and selective precipitation. In this work, (1-4)-a-L-guluronan oligomers extracted from alginate were used as building blocks in the synthesis of biohybrid glycopolymers and chimeric polysaccharides with original gelation properties characterized by rheology.

Biohybrid glycopolymers. The starting oligosaccharides were transformed into macromonomers by introducing a methacrylamide group at their reducing end (Figure 1). They were then copolymerized with 2-hydroxyethylmethacrylamide (HEMAm) either by conventional radical or by RAFT polymerization. In both cases, the oligosaccharide content was 20-50% by mass. After purification by diafiltration, the graft copolymers were redissolved in water and dialyzed against CaCl2. Poly(HEMAm-co-GulA20MAm) gives a soft self-standing transparent hydrogel (Figure 2a).

Chimeric polysaccharides. The same rationale was followed for the design of chimeric polysaccharides: When (1-4)-a-L-guluronan chains (DP=20) were grafted onto a biocompatible and biodegradable polysaccharide, the resulting polymer formed a soft elastic self-standing hydrogel upon dialysis against CaCl2.

The use of both types of hydrogels in biomedical domain and in 3D cell culture application is envisaged.

Figure 1. Macromonomer based on oligo-guluronate.
Abnormal Elution Of High Molecular Weight Polysaccharides Using Size Exclusion Chromatography

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Abstract

Polysaccharides are of interest in many application domains due to their rheological properties. Indeed, they can be used in low concentrations as a thickening agent, due to their ability to increase the viscosity of a solution / product. Their properties are related to important characteristics of the macromolecules such as the chemical composition or the ionization degree but mostly their molecular weight. To define this latter characteristic, different separation techniques based on the size and coupled with a MultiAngle Laser Light Scattering (MALLS) can be used like Size Exclusion Chromatography (SEC), HydroDynamic Chromatography (HDC) as well as Asymmetric Flow Field Flow Fractionation (A4F).

Pasch et al. have shown that according to the flow rate the use of HDC (non-porous bead) could lead to an abnormal elution of High Molecular Weight Polymers (HMWP).[1] This is also called Slalom Chromatography mode. In this case, HMWP are eluted after smaller ones, i.e the expected elution order is inverted due to the coil-stretch transition of HMWP. This feature can be predicted by the determination of the Deborah number corresponding to the product of the longest relaxation time of the polymer, which depends on the radius of gyration, the viscosity and the temperature, and the strain rate of the flow, which depends on flow rate, particle size and characteristics of the stationary phase.

In the present work, the behavior of dilute solutions of HMWP flowing within a porous bead (particle size ranging from 10 to 60 µm) will be presented. To this end, a dextran of 400 000 000 g/mol (from INS A, Toulouse) was used as a macromolecular model.[2] After hydrolysis, a large range of sizes of dextran was obtained, allowing the observation of the abnormal elution limit, according flow rates and size of the macromolecules. Results obtained on SEC/MALLS will be compared to published A4F results.

References
Multiple-Particle Tracking Study Of The Microheterogeneity Of β-Glucan-Rich Hydrocolloidal Extractive Suspensions

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Abstract

Nutrim-10 is a newly developed food product containing the dietary of soluble fiber β-glucan. The micro-structural heterogeneities of Nutrim-10 suspensions were investigated by monitoring the thermally driven displacements of well-dispersed microspheres via video fluorescence microscopy. By comparing the distribution of the time-dependent mean-square displacement (MSD) of polystyrene microspheres embedded in three concentrations of Nutrim-10 suspensions, we found that the degree of heterogeneity of the suspensions increased dramatically within a narrow range of Nutrim-10 concentrations. The ensemble-averaged MSD of 5.5% Nutrim-10 suspension exhibited a power-law behavior which scaled linearly with time. This behavior was similar to that of homogeneous aqueous glycerol solution. But the MSD distribution was wider and more asymmetric than for glycerol. Increasing Nutrim-10 concentration rendered the MSD distribution much more asymmetric and skewed. Multiple-Particle Tracking (MPT) provided a new and quantitative method to characterize the organization of plant biopolymers in suspension or solution.
Characterization Of A New Sulfonated, High Temperature Polymer For Use In Hydrogen Fuel Cells

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Abstract

The need for more efficient and reliable fuel cells has resulted in the synthesis and evaluation of a number of high temperature polymers which can be incorporated into proton exchange membranes. The polymers investigated range from polyether (ether) ketones (PEEK) to sulfonated polyphenylquinoxalines (PPQ) (1). The utility of each group of polymers was measured by end-use tests such as water uptake and ionic conductivity. While these tests are useful for differentiating the various polymeric candidates, information about the chemical structures of the various isomers of each polymer group has proven to be difficult to obtain. Also lacking is a simple analytical method for monitoring the progress of the synthesis, in near real time.

This report describes an analytical system which can be used to rapidly characterize a polymer based upon its thermal profile and the identification of compounds present in each thermal zone. The analytical system consists of a multi-functional pyrolyzer interfaced directly to the split/splitless injection port. The vapors from the polymer flow through the splitter into a high resolution, high temperate capillary column. The now-separated constituents of the vapor then flow directly to the ion source of an electron impact mass spectrometer. The multifunctional pyrolyzer can be programmed to function in a number of different modes. These include evolved gas analysis, flash pyrolysis and selective sampling of each EGA thermal zone. A newly synthesized polymer designed for use in a new proton exchange membrane was evaluated using all three analytical modes mentioned above.

The polymer was analyzed directly; no conventional solvent based sample prep was needed. Microgram quantities of the polymer were placed in an 80 µL deactivated sample cup which was then placed in the auto sampler carousel.

Evolved gas analysis (EGA) is the first step. EGA-MS produces a thermogram. This thermogram provides a "picture" of the sample’s complexity. “Features” seen in the thermogram guide the analyst for the next steps in the “method map”. The EGA thermogram of this experimental polymer was generated by heating it from 100 to 800 °C @20 °C/min. There are four distinct thermal zones in the EGA thermogram. Each zone is isolated and analyzed using advanced heart-cutting techniques. Four different total ion chromatograms provide information about the boiling point distribution of the constituents of the entire polymer.

The membrane was also examined using flash pyrolysis at 700 °C. This temperature was used because the EGA profile clearly shows that the organic degradation of the polymer is complete at 700 °C. Many pyrolyzates are formed; each represents a part of the polymer structure. Identification of the individual pyrolyzates is made using the mass spectrum of each peak and the search results of the NIST mass spectra library. The sample is tentatively identified as sulfonated polyphenylquinoxaline based upon the mass spectral identifications and the detection of SO2 from the membrane sample at elevated temperatures.
Stimuli Responsive Ultrahydrophobic Polymer Surfaces Synthesis, Characterization And Application

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Abstract

The Ultrahydrophobic properties of a lotus leaf are well known and are based on a hierarchal multifunctional polymer surface structure in the µm and nm range. To mimic and potentially improve on this natural phenomenon is an appropriate challenge for polymer science. The lotus leaf surface can be perfectly modeled by the use of a polymer particle in the µm range and a polymer coating in the nm range.

Multifunctional polymer surfaces based on the hierarchal surface, show ultrahydrophobic and superhydrophilic behavior. To realize multifunctionality it is necessary therefore, to combine different functionalities in one material or in this case in one polymer molecule. Superhydrophilic and ultrahydrophobic surface behavior was achieved using µm based hierarchical silica particles and nm scaled polymer surface structure. This involves the production of core-shell-nanoparticle layers on a variety of substrates such as polymers and metals to produce materials with easy-to-clean (anti-soil and anti-stain behavior) and self cleaning properties.

The synthesis of tri block copolymers using controlled living polymerization techniques and the preparation of the core-shell-nanoparticles to produce polymer "brushes" will be presented. Using these polymers as examples, modern 2D _FTIR coupling techniques were used to determine the molar mass and the composition of the polymers.

The synthesised triblock-copolymers consist of a block responsible for the anchoring to the substrate, a “hydrophilic” and a “hydrophobic” block. This offers the possibility to combine responsive switching of the wettability behavior and the anchoring to a substrate in one molecule. The wetting behavior of the brushes can be switched by external stimuli: temperature, pH, solvent polarity, salt concentration etc.

The properties will be discussed with respect to the surface density the copolymer composition and the block lengths.

Applications for the possible industrial use of these new surface properties will be shown.

We acknowledge funding by BMBF (project UltraSurf 02PU245).
Determination Of Inorganic Elements In Brazilian Oxo-Biodegradable Plastics By Neutron Activation Analysis

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Abstract

Concerns about the accumulation of plastic waste and its consequent environmental impact have led scientists and the chemical industry to search for degradable polymers, as natural biopolymers or synthetic polymers with additives which facilitate degradation, known as oxo-biodegradable plastic. Due to production processes and the use of additives and dyes, some plastics often contain small amounts of chemical elements that are not part of the polymer molecules.

Oxo-biodegradable plastics are synthetic polymers into which have been incorporated light-sensitive chemical additives with the objective of initiate or accelerate the biodegradation process by photodegradation, through oxidation and molecular weight reduction. These two processes allow the plastic to become weak and fragile and biodegraded. In Brazil, for some time now, packs and bags labeled oxo-biodegradable, containing a specific additive, have been distributed in shops and supermarkets.

Therefore, with the beginning of the industrial production and commercial application of degradable plastics, the determination of inorganic constituents present in these materials became of paramount importance. Degradable plastic containing significant amounts of chemical elements like As, Br, Cd, Co, Cr, Fe, Sb, Sc, Se and Zn, may be inappropriate for commercial uses. They may also become soil and water pollutants, since during degradation of the polymeric material these chemical elements can be deposited in the environment where the plastic has been discarded.

Neutron activation analysis (NAA), a primary method of measurement, was selected for the quantification of chemical elements in the polymer samples. This method is based on the detection of radiation emitted by atomic nuclei present in the sample that are converted into radionuclides by nuclear reactions caused by neutron bombardment.

Plastic bag samples were collected directly in shopping facilities of São Paulo state. Preparation included thorough washing and separation of the parties without graphic prints. Analytical portions of 200 mg of the selected material were packed into high purity polyethylene capsules and irradiated in the nuclear research reactor at the Nuclear and Energy Research Institute (IPEN), in São Paulo, SP. Certified reference materials (ERM-EC 680k and ERM-EC 681k) were irradiated together the samples for quality control purposes.

The detection of induced radioactivity in the samples, certified reference materials and analytical blanks was performed in high resolution gamma ray spectrometers with hyperpure germanium detectors, located at the Radioisotopes Laboratory, Nuclear Energy Center for Agriculture (CENA/USP), in Piracicaba, SP. Mass fractions values and respective uncertainties were obtained by k0 standardization method.

Because of its nondestructive nature, NAA proved to be convenient for analysis of polymer samples in solid state, thereby not requiring any chemical treatment. Also its multielementary characteristic allows a prospective analysis of the samples as can be seen in Figure 1. It is expected that this study contributes with important information about the composition of oxo-biodegradable polymers currently produced in Brazil.
Gamma ray spectrum showing some elements found in one of the oxo-biodegradable polyethylene samples.
Utility Of Chromatographic And Spectroscopic Techniques For Detailed Characterization Of Complex Macromolecules

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Abstract

We present detailed characterization of a protein-PEG conjugate using two separation techniques, i.e., asymmetrical-flow field-flow fractionation (AF4) and size-exclusion chromatography (SEC), which were on-line coupled to a series of successively connected detectors: an ultra-violet, a multi-angle light-scattering, a quasi-elastic light-scattering, and a refractive-index detector (UV-MALS(QELS)-RI). Matrix-assisted laser-desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was used as a complementary characterization technique. The aim was to determine the molar mass and the chemical composition of the conjugate as well as the presence of residual un-reacted protein and/or PEG reagent in conjugate sample. In addition, the presence of high molar mass aggregates in solution was studied in dependence of the type of buffer solution in which the conjugate was stored. The second part comprises a detailed characterization of poly(styrene-b-isoprene) (PS(PI)x) miktoarm star copolymers synthesized by anionic polymerization of polystyrene (PS) and polyisoprene (PI) blocks and selective chlorosilane coupling chemistry. The PS(PI)x star copolymers consisted of one long PS block and different number of shorter PI blocks (x = 2, 3, 5 and 7). PS(PI)x star copolymers differed also in the length of PI block, which decreased with the number of PI blocks in the star copolymer. Our aim was to determine the purity of samples and to identify exactly the constituents of individual samples. For this purpose we used a variety of separation techniques (size-exclusion chromatography (SEC), reversed-phase liquid-adsorption chromatography (RP-LAC) and two-dimensional liquid chromatography (2D-LC)), and characterization techniques (UV-MALS-RI multi-detection SEC system, NMR and MALDI-TOF MS).

The results of our research work show that detailed characterization of complex polymers requires a comprehensive study, comprising not only the spectroscopic techniques but also efficient chromatographic techniques hypenated with multi-detection systems.

Characterization Of A Non-Ionic, Water Soluble, Helical, Rod-Like Polymer

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Abstract

Rod-like polymers lend themselves towards theoretical endeavors because they have a rudimentary morphology. Although there are many rod-like polymers, they typically are ionic or are soluble only in difficult to work with solvents. As an example, poly(benzyl-g-L-glutamate), a rigorously studied rigid rod, is only soluble in hygroscopic solvents, but will aggregate at low concentrations of water. Alternatively, not inherently bad, ionic interactions are less than desirable for simplicity sake; Therefore, a non-ionic, water soluble, helical, rigid rod was synthesized. Poly(PEG-lysine), a lyotropic and highly helical polymer, was characterized by GPC with multiple-angle light scattering and DLS. This work was supported by NSF award 1005707 (DMR).
Understanding Branching Heterogeneity Of C60 Core Star Polymers By Temperature Gradient Interaction Chromatography

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Abstract

Polymer chemists have traditionally relied on Size Exclusion Chromatography (SEC) to provide information about the heterogeneity in synthetic polymer samples. Unfortunately, SEC separates based on the hydrodynamic size of a molecule, which is dependent on the polymer architecture, chemical make-up and other factors. Temperature gradient interaction chromatography (TGIC) offers an advantage because separation is based on the balance of enthalpic interactions between the polymer and solute and between the polymer and stationary phase, which to a first approximation scale with the degree of polymerization. The grafting of polymeric organolithium compounds to fullerenes has been reported to produce well-defined star shaped polymers with an upper limit of six arms per fullerene. Recent reinvestigation of the products of this reaction by TGIC reveal a significantly more heterogeneous product distribution than previously thought. Off-line SEC analysis with both viscometry and light scattering detectors coupled with an analysis based on branching from a central core is used to characterize the distribution of products.
Original Mechanical Characterization Of Single Micrometric Vesicle By Atomic Force Microscopy

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Abstract

The study of soft particle deformation is of paramount importance for the advancement of fundamental colloidal science as well as its biomedical applications, particularly in drug delivery and cell mechanics. Recent developments of both theoretical modeling and experimental techniques have made it possible to measure the deformation behavior of a single micro-/nano-particle (e.g. polyelectrolyte capsules, cells…) under compressive deformation and, therefore, to characterize its mechanical and interfacial properties [1].

We have already shown that the interactions of lipid membranes with water-soluble polymers play a role on vesicles mechanical properties [2]. Since cell mechanical properties are of great importance in the first steps of biological processes, we have decided to further study the role of membrane coating by a polymer on GUVs deformation. We have used a zwitterionic fluid lipid (DOPC) and a positively-charged polyelectrolyte: the chitosan.

This work reports the first extensive characterization of a fluid lipid membrane using the compression between two planes of isolated Giant Unilamellar Vesicles (radius > 1 µm). Reproducible and reversible force-deformation curves for individual GUV are obtained and reveal a radius-dependency of the liposome force response. Effective bending and stretching moduli of lipidic membranes are then simultaneously determined using a simple elastic model [3] for bare and chitosan coated GUVs [2,4]. Our original analysis illustrates the influence of a charged macromolecule-lipid membrane interaction on its mechanical parameters, and highlights the marked sensitivity of this method to investigate soft objects.

References
Abstract

Organic polymers are often used as barriers to the transport of diffusing species. At constant temperature and pressure, the diffusion rate of carbon dioxide and hydrogen sulphide through polymers or elastomers can reach a steady state. Factors that affect the transport rate, such as the temperature and pressure history, are of interest in many applications.

In this study, polyphenylene sulfide has been exposed to supercritical CO2 at 100 bar and 100ºC in a permeameter. The temperature was then reduced to 90ºC and the transport rate determined. In a separate experiment the temperature was reduced to 90ºC and the pressure was reduced to atmospheric in 2 minutes. The transport rate was then determined when the sample was tested at 90ºC. These results have been compared with data from samples that were taken above the glass transition temperature in the absence of supercritical CO2. Similar experiments were also carried out for fluoroelastomers.

After each test the samples were analysed using FTIR microscopy, differential scanning calorimetry (DSC) and X-ray diffraction.
Probing Industrial Polymer Compositions Using Liquid Chromatography Coupled To Infrared Spectroscopy Detection

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Abstract

Analytical analysis of polymers in an industrial setting typically includes determination of the molecular weight distribution using gel permeation chromatography (GPC). However, if a copolymer or polymer blend is studied it can be difficult to determine the contributions from the different species present or spreads in composition across a given molecular weight distribution. The LCIR is an instrument which couples liquid chromatography separations with real time Fourier transform infrared spectroscopy (FTIR) detection. The ability to monitor the change of the IR spectrum across polymer LC separations has allowed us to reach greater depth in polymer composition analysis. Small molecules have been discovered, such as contaminants, which would not be identified through typical detection techniques (UV, RI, etc). Additionally, compositional changes across molecular weight distributions have been established by coupling GPC to FTIR detection. This helps to elucidate compositional drift in a copolymer distribution which is important in understanding the effects on the physical and mechanical properties of the sample and allows optimization of the process chemistry conditions as a function of the intended application. Although the technique for real time deposition through a solvent removal interface is new and method development is required for a given mobile phase, the rich compositional information afforded by the LCIR makes it an invaluable instrument for polymer analysis.
Adaptation Of Automatic Continuous Online Monitoring Of Polymerization Reactions (ACOMP) to Industrial Scale Reactors

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Abstract

ACOMP is a mature laboratory instrumentation and analysis platform for monitoring many characteristics of polymerization reactions while they occur. The method has been adapted to a wide variety of reactions, including free radical and controlled radical copolymerization, condensation reactions, post-polymerization functionalization, natural product modifications, and more. It has been used in solvent, bulk, and inhomogeneous reactions, including emulsions and inverse emulsions, and in pressurized, high temperature, and high viscosity reactions. Its utility has been demonstrated for batch, semi-batch, and continuous reactions. The primary application has been in determining fundamental mechanisms and kinetics of polymerization reactions and for optimization of reaction and process conditions, including predictive control of molecular weight and copolymer composition. An ongoing development, sometimes termed ‘second generation ACOMP’ allows monitoring the onset and evolution of polymer stimuli responsiveness during ‘smart polymer’ synthesis.

Here, developments and challenges in a major ACOMP frontier are considered; the adaptation of ACOMP to full scale industrial reactors. Full scale implementation at the industrial level will lead to important efficiency gains in the use of energy, non-renewable resources and feedstocks, plant and labor time, and to higher product quality, less emissions, and greater worker safety. The overall effect will be the reduction of the environmental footprint of the polymer manufacturing industry.

The contrasts in the requirements for ACOMP in the R&D laboratory versus the industrial milieu are quite poignant. For example, for R&D use ACOMP normally seeks the maximum number of different detectors to produce massive data streams that can be analyzed to give a multifold picture of the reaction process. For an industrial use, however, one seeks the least number of detectors to characterize only the most necessary reaction characteristics, e.g. polymer molecular mass and residual monomer concentration, in the simplest and most reliable fashion possible. In the industrial ACOMP, robustness and redundancy of the ACOMP ‘front-end, detection,’ and analysis is also a new dimension. Various engineering and design challenges are outlined in this presentation, as well as steps towards the ultimate integration of ACOMP into full closed loop feedback control of industrial scale polymerization reactions.
Inferring CCD Using Crystaf - Uncertainty Analysis

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Abstract

Several methods have been used to measure chain crystallizability in semi-crystalline polymers – Crystaf being the most common. These crystallization profiles obtained from Crystaf are converted to chemical composition distribution (CCD) using different methods. The conventional way of converting Crystaf profiles to CCD uses a calibration curve that correlates crystallization peak temperature and average comonomer content. This method is a tedious experimental approach since calibration curves depend strongly on operation conditions. Anantawaraskul et al. (S. Anantawaraskul, P. Somnukguandee, J. B. P. Soares, and J. Limtrakul. Application of a crystallization kinetics model to simulate the effect of operation conditions on Crystaf profiles and calibration curves. J. Polym. Sci. Part B, 47(9):866(876, 2009) proposed a method based on kinetic model for constructing Crystaf calibration curves, which, in principle, reduces the experimental load. In our current work we perform an uncertainty analysis of this approach. The goal of this work is to determine not only the CCD that corresponds to an obtained Crystaf profile, but also the associated confidence intervals, given the imperfections in the model and experiment.
Detailed Characterization Of The Composition And Morphology Of Polystyrene-B-Poly(Ethylene Oxide)-B-Polystyrene Of Interest As Solid Electrolytes For Lithium Batteries


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Abstract

The research on electrochemical storage of energy is today in a stage of fast and profound evolution owing to the strong development of portable electronics requesting power energy as well as the requirement of greener transport modes (hybrid and full electric vehicles, better energy management in air and railroad transport). Most commercial batteries use liquid or liquid-based electrolytes, which limits their thermal stability, energy density and safety (short circuits leading to the explosion of the battery). These limitations could be considerably offset by the use of solid polymer electrolytes (SPE). The latter would also be compatible with lithium metal as anode, which is the ultimate negative electrode for the design of storage systems with high energy density. Thus, lithium metal polymer technology would be a major innovation in this field. However, the main drawback of the SPE is the decrease of the ionic conductivity with increasing mechanical strength, necessary to avoid the formation of lithium dendrites during the recharge of the battery, thanks to their capacity to self-assemble at a nanometer scale. A solution consist in developing electrolytes from block copolymers, which are able to combine in the same material these two antagonist properties (mechanical and conductivity)[1,2].

Recently, we have demonstrated that triblock copolymers polystyrene-b-poly(ethylene oxide)-b-polystyrene (PS-b-PEO-b-PS)[3] with a poly(ethylene oxide) block as ionic conductor and polystyrene block providing mechanical strength was a promising candidate as SPE. In order to build composition/morphology/performance relationships, our aim is to determine carefully the composition and the nanostructuration of the polymer.

In this communication we will present our latest results about the composition characterization of the previously prepared PS-b-PEO-b-PS using liquid chromatography, namely Liquid Chromatography at Critical Conditions (LCCC)[4] and Liquid Chromatography under Limiting Conditions of Desorption (LC LCD)[5]. Furthermore, analyses of morphologies and nano-structure by Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Small Angle X-ray Scattering (SAXS) techniques will be also discussed. Interestingly, we noticed that the presence of residual PEO even at a very low concentration impacts strongly the organization of the triblock copolymers.

Thermal Degradation Kinetics Of Un-Irradiated And High Energy Proton Irradiated Polyvinyl Butyral

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Abstract

Polymers have garnered the interest of researchers worldwide in various fields of science and technology. The reason that, besides having excellent inherent properties, their characteristics can be altered to suit specific requirements by various treatments e.g. chemical doping, heat treatment, ion implantation. One of the methods of modification, like upgrading, stabilization and changing the properties of polymers is based on the irradiation with high energy accelerated radiation (gamma rays, X-rays, and accelerated ion beams). Irradiation of polymers with high energy radiations leads to the formation of very reactive intermediates in the forms of excited states, such as ions and free radicals. These intermediate forms are almost instantaneously used up in several reaction pathways which result in the arrangement or formation of new bonds structures. The ultimate effects of these reactions are the formation of oxidized products, grafts, cross-linking and scissoring of main or side chains. A comparative study on thermal degradation kinetics of un-irradiated and high energy protons irradiated polyvinyl butyral (PVB) was investigated based on weight loss analysis and non-isothermal approaches. Thermogravimetric analysis reveals that due to high energy protons irradiation exposure following by chemical etching, the thermal stability of the PVB film is increased significantly. The weight loss by the un-irradiated PVB upon heating was found to be in two stages and due to high energy protons accelerated exposure, this weight loss transition proceeds in a major one stage with increases in the highest rate of weight loss temperature. Chemical etching of the irradiated PVB film leads to further increasing of this weight loss temperature transition. In addition the samples were analyzed by FT-IR for illustrating the stability of irradiated and chemical etched samples. The kinetic triplet and other related kinetic parameters were analyzed and compared for un-irradiated, irradiated and chemical etched PVB.
Characterization Of Chemical Composition Heterogeneities In Polyolefins Using Two-Dimensional Liquid Chromatography With Online Infrared Absorbance Detector

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Abstract

Adsorption liquid chromatography is able to fractionate polyolefins with different chemical compositions. A polymer sample is injected onto a graphitic carbon column (Hypercarb™) filled with adsorption promoting solvent (weak eluent). The composition of the solvent is then changed by increasing the content of a desorbing solvent (strong eluent). The adsorbed polymer components are desorbed according to the affinity with the column. The components with high ethylene content elute later than those with low ethylene content.

The gradient prohibits the use of concentration detectors, such as refractive index and infrared detectors, being connected with the HPLC column. An evaporative light scattering detector (ELSD) is commonly used but its response is not linear. Therefore, it is difficult to achieve quantitative results. The study here reports an approach to overcome the problem by connecting the HPLC column to a second dimension GPC column. The polymer components after HPLC separation are analyzed online by the GPC column. The GPC column is connected with both light scattering and infrared detectors. The infrared detector provides both the concentration and composition measurements of HPLC fractions. The addition of light scattering signal yields absolute molecular weights of the fractions.
Preparation And Characterization Of Swift Heavy Ion Beam Irradiated Polycarbonate/ Zinc Oxide Nanocomposites Films

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Abstract

Polycarbonate (PC)/Zinc oxide (ZnO) nanocomposite samples are prepared by a solution mixing method. The amorphous ZnO nanopowder of particle size 80nm is used as a nanofiller in PC matrix. The samples were kept in vacuum for 24h to remove the effect of volatile solvent. Vacuum dried samples were irradiated by 55 MeV carbon ion beam at various ion fluences ranging from $1 \times 10^{11}$ to $1 \times 10^{13}$. The structural morphological properties are studied by employing scanning electron microscopy (SEM), energy dispersive X-ray spectra (EDX), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). EDX spectra indicate the presence of ZnO on the surface of the nanocomposite films. The XRD pattern reveals that the average crystallite size and percentage of crystallinity decrease with increases of ion fluences. FTIR spectra reveal the position of different bonds in PC and nanocomposite films. The glass transition temperature was found to be decreases with increase in ion fluence. The addition of ZnO in PC matrix and its irradiation causes the increase in amorphousity of PC is the reason behind decrease of glass transition temperature. It is investigated that the amorphous nature of nanocomposite film increases with increase of ions fluences due to chain scissoring/cross-linking or electronics energy loss.
Characterization And Comparative Study Of Polymers Used As Viscosity Index Improvers For Automotive Lubricant Oils

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Abstract

Viscosity Index Improvers (VIIs) are among the most important additives used for automotive lubricant oil formulation. In this study, eight commercial VIIs based on poly(styrene-co-isoprene) hydrogenated - viscosity modifiers serie A - and poly(alkyl methacrylate) – viscosity modifiers serie B, have been characterized by Thermogravimetric Analysis (TG), Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). It was observed that the VIIs, based on poly(styrene-co-isoprene) hydrogenated, have higher thermal stability than the VIIs based on poly(alkyl methacrylate), but both are suitable for use in automotive engines. However, it should be noted that the commercial MIVs series B were supplied in diluted oil. This fact could have influenced the degradation temperature of the samples. The main absorption bands of the VIIs analyzed were identified by FTIR analysis. The influence of VIIs on the characteristics of lubricating oils was evaluated through kinematic viscosity tests, calculation of viscosity index and study of the rheological behavior. Light and medium parafinic base oil were additivated with two types of VIIs, from serie A, A2 and A5 types, at different concentrations. It was observed that the parafinic oils are good solvents for both additives. The kinematic viscosity of additivated parafinic base oils increased with increasing concentration of VII. A5 showed the greatest thickening effect due to its polymer molecular structure, specially the number of styrene blocks. For all the studied concentrations, there was a significantly increase on the viscosity index (VI) of the samples in comparison with the pure oils. MIV A5 showed better performance than MIV A2, allowing the use of a smaller amount of additive to achieve the same IV. Light and medium parafinic base oil additivated with A2 and A5, in different concentrations, showed, predominantly, viscous behavior, and good stability to deformation. It was observed that additivated parafinic base oils exhibited non-Newtonian behavior. This behavior was better described by the Power Law of Ostwald de Waele. From Creep / Recovery tests, it was verified that an increase in additive concentration, for a given time value, caused a decrease in the value of compliance. This fact was attributed to the presence of polymer, that even at low concentrations, provides increased resistance to deformation to an applied stress. It was observed the dependence of complex viscosity (\(\eta^*\)) on temperature for additivated parafinic base oils. The complex viscosity decreased with increasing temperature, particularly in samples with high concentration of additive. However, it remained, for all polymer concentrations studied, in the temperature range considered, in amounts exceeding those of pure oils, attesting the effectiveness of the additives serie A as VIIs.
Rheological Characterization Of Gum Polymers Using Rotational And Oscillation Tests

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Abstract

The rheological properties of gum polysaccharides are a direct effect of their structural features and the conformation they assume when they dissolve in water. Texturizing properties such as their thickening, water binding, gelling and film forming can be explained largely by the differences in their structural and molecular features. Individually, these gum polymers have their own unique properties that can be differentiated by their viscosities and visual flow characteristics. Their rheological characteristics, whether they show Newtonian flow, a strong pseudoplastic or less pseudoplastic flow, or if they will behave more as a viscoelastic solid or a viscoelastic liquid vary with individual gums and their concentration in water. Flow curves and amplitude sweeps of various gum polysaccharides were analyzed using an air-bearinged, parallel plate rheometer in rotational and oscillation test modes, respectively. Branched, anionic gum polymer such as gum arabic which has a globular structure and a smooth visual flow, showed a Newtonian flow up to a concentration of 40% w/w and very slightly pseudoplastic flow up to 55% w/w with flow behavior index of 0.93 or higher; its amplitude sweeps revealed a viscoelastic liquid behavior up to 55% w/w [corresponding to solution viscosities of 50 mPa.s to 5000 mPa.s @20 RPM] where loss modulus G? curves ran higher than the storage modulus G'. On the contrary, xanthan gum, a five-fold helix with a gel-like snotty visual flow, showed a highly pseudoplastic behavior with flow behavior index ranging from 0.36 to 0.11 for 0.07%-2.25% w/w xanthan concentration in water. Its amplitude sweeps revealed a totally different behavior, i.e. at 0.07% w/w [corresponding to 50 mPa.s @20 RPM], xanthan initially had a viscoelastic liquid character where its loss modulus (G?) curve starts higher than its storage modulus (G’) curve, then it crosses over at shear strain around 1% and switching to a viscoelastic solid. At concentrations of 0.32% w/w and higher [500 mPa.s to 5000 mPa.s @20 RPM], xanthan distinctly transitioned into a viscoelastic solid where G’ curves are widely separated from their corresponding G? curves. This same behavior was shown by colloidal MCC that have a similar gel-like flow like xanthan. The two-fold helical, anionic, more polar and more water soluble gums such as lambda-carrageenan, sodium alginate and low molecular CMC gave flow behavior indices lower than gum arabic of 0.75 to 0.8 for each solution viscosity of 500 mPa.s @20 RPM [concentrations of 1-4% w/w]; their amplitude sweeps showing viscoelastic liquid behavior like gum arabic at solution viscosities of 50 mPa.s to 5000 mPa.s @20 RPM. The two-fold, neutral gums such as konjac, guar gum, locust bean gum, and HPMC gave flow behavior indices of 0.45 to 0.70 at each solution viscosity of 500 mPa.s [concentrations of 0.27-0.87% w/w]; their amplitude sweeps revealed a different behavior, i.e, a viscoelastic liquid behavior at solution viscosities up to 500 mPa.s @20 RPM and transitioned to viscoelastic solid at solution viscosities of 5000 mPa.s @20 RPM.
Blown Film Stability Of Bimodal Polyethylene Resins

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Abstract

The present study investigates the relation between the molecular weight distribution (MWD), as well as the molecular weight between entanglements (Me), as by obtained by the Plateau modulus with the bubble stability index for the blown film process of 6 bimodal, high density polyethylene (HDPE) resins.

Characterization of all resins were performed including, oscillatory rheometry data, shear and elongational viscosities, relaxation modulus, as well as melt flow index (MFI) measurements. Molecular weight distribution was deconvoluted to analyze the effect of the low molecular weight and the high molecular weight portions.

It was found that some molecular weight indices of the deconvoluted molecular weight distribution of the resins were related to the bubble stability index.
Polyolefin Characterization By Diffusion Ordered NMR Spectroscopy

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Abstract

Diffusion ordered Spectroscopy (DOSY) is one of the most powerful NMR technique and able to separate multicomponent material without using chromatographic / other separation/fractionation techniques. The basic principle is based on the application of magnetic field gradient pulse & observation of decrease in NMR signal as function of gradient strength. A signal due to small molecule (i.e. higher diffusion co-efficient ) disappears with application of small gradient strength, whereas the signal from large molecule remains intact. Therefore NMR signal can be easily separated depending on the size or molecular weights of different components of materials under study. Although there are several publications on DOSY, but there are limited applications to polyolefins. Due to lack of low temperature solubility of polyolefins, the major issue is convection flow in a sample tube during high temperature measurement with DOSY. The mobility of molecules under study will not only due to their self diffusion but also by macroscopic convection flow & leads to meaningless DOSY data. After examining several experimental conditions, we could establish a method to obtain a meaningful high temperature DOSY spectrum of polyolefins. Double stimulated echo pulse sequence was applied for achieving good quality DOSY spectrum alongwith the avoidance of convection flow at high temperature. Examples of Homo- & Co-Polyolefins will be presented.
Polyolefin Microstructure Analysis Via Triple Detector HT GPC Combined With FT IR Detection

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Abstract

The dynamic polyolefin market requires complicated microstructures to fulfill the needs of specific applications. A recent trend in the polyolefin industry is developing resins with bimodal or multiple modal molecular weight distributions (MWD) and bimodal or multiple densities (co-monomer content distribution CCD). These resins are created either using post production blending, dual reactor processes, or single reactor dual/multiple catalyst processes.

Detailed structural information of these resins and the correlation between the structures and their performance are keys to the future success of any polyolefin business. Combining a triple detector HT GPC with a full spectrum FT IR provides strong polyolefin analysis capabilities. The triple detector HT GPC analyzes polyolefins MW/MWD, as well as branching information.[1] The DiscovIR, with solvent removal, provides instant analysis of the compositions of polyolefin and additives.[2]

Two commercial instruments, triple detector high temperature GPC from Malvern (Malvern HT 350a) and a FT IR deposition and detection system from Spectra Analysis (DiscovIR-LCTM) were connected through a creative design. Polyolefin sample eluted from the GPC columns were either analyzed through the triple detector (dRI, Viscometer, LALLS), or analyzed by the FT IR after the sample was deposited continuously onto an IR transparent disk. The switch between the two analysis techniques was freely performed and controlled by computer. Complicated polyolefin systems were analyzed with this system. Further analysis of the polyolefin deposit can be performed by an FT IR microscope where one can obtain more detailed compositional information at low concentrations in certain elution fractions.

References:
Application Of Malvern Polyolefin Characterization Technologies For The Process Control Of UHMW Polyethylene Resins And Fibers

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Abstract

Ultra High Molecular Weight Polyethylene (UHMWPE) is a high performance version of the world’s most popular synthetic polymer called Polyethylene and is classified as an engineering plastic. Due to the higher value added aspect of this class of materials, the quality control requirements are critical to the delivery of consistent performance specifications. One of the key control parameter is Intrinsic Viscosity (IV) which is traditionally done by some type of Glass Capillary measurement. IV is an important molecular parameter because it provides an estimate of the molecular weights and a direct correlation with physical properties of various resins and fibers. Excellent precision and accuracy results will be shown for this exclusive Malvern High Temperature Dilute Solution Viscometer (HT-DSV). Another important control parameter is the measurement of residual solvent levels in the fibers. A combination of extraction techniques is required to measure the external as well as internal solvent residues which are critical for the optimization of fiber strength. We will show how a modified Malvern Xylene Solubles technology provided the accurate analysis without interference from the wax component of polyethylene.
The Development Of A Multi-Angle-Light-Scattering Detector For Field Characterization Of Proteins Macromolecules And Particles Using Either Flow Fractionation Or Size Exclusion Chromatography

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Postnova Analytics

Abstract

The challenges that faced the engineers in the 1940s through to 1970s was the ability to develop systems for the characterization of the Molecular Weight and Size that matched the excellent mathematically derived equations that described the properties of the macromolecules. These instruments were large and precise but were victim of the available technology at the time, The 60s-70s brought on the advent of gas lasers that led to Gonimeters and Flow through systems. The design of these systems was driven by the expected type of applications that would require characterization, the analysis of high molecular weight polymers were determined to by low angle light scattering where the angle is so close the zero angle that the determination macromolecules could be carried out accurately. With these new system the user could be confident that the values determined would be accurate. In the early 90s the inexpensive diode lasers became available with this innovation and the introduction of fixed multi angle a detectors, where an array angles were used to extrapolate to the zero angle. Or in the case of isotropic scatterers any angle could be used. The ability to characterize a wide range of proteins and polymers became a normal procedure in most polymer and protein laboratories. In recent years the characterization of colloids and larger particles have become important and now with the more recent introduction of nanoparticles the challenges faced by Field Flow Fractionation and Size Exclusion users have become challenging. This paper proposes to examine how the improvements in design of a multi angle lights cattering detectors can improve how Scientists to determine mass and size accurately of a greater array of molecules and now nano-particles. The paper will also examine some of the challenges still facing instrument designers with respect to the limitations of MALS when characterizing very dense nano-particles.
Preparation And Characterization Of Doxorubicin HCl Loaded Chitosan Nanoparticles Prepared By W/O Emulsion Method

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Abstract

The aim of present investigation was to prepare and evaluate chitosan nanoparticles containing doxorubicin by w/o emulsion method. The prepared particles were characterized for the particle size distribution, Scanning electron microscopy, and Thermal analysis by DSC and IR spectrum for the drug and polymer interaction and compatibility. SEM indicated spherical structure of nanoparticle without agglomeration. FTIR spectra indicated no chemical interaction between drug and polymer. In vitro drug release study suggests sustain drug release for longer period of time. Vigorous agitation leads to formation of smaller particle which lies in nano size and its drug release study confirms its sustained release.
Poster Presentation Abstracts
PHB/PCL Blend – Organo Clay Nanocomposites Obtained By Film Extrusion Evaluation Of Morphology by TEM and SAXS

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Abstract

In recent years, it has been shown that the presence of clays modified with organic salts in polymeric compounds may improve their properties, and also act as emulsifier in immiscible polymer blends. In previous work, we studied the blend of two biodegradable polyesters, PHB, a fragile polymer, and PCL, with ductile behavior and low melting temperature. Physical mixture of these polyesters can balance their physical properties to obtain a biodegradable, environmentally friendly material.

Extrusion technologies represent the major process of the thermoplastics industry, and play an important role in many related industries. The aim of this work is to study the effect of added an organo-modified montmorillonite on the morphology of PHB/PCL polymer blend obtained by twin screw extrusion followed by cast film extrusion. Blend morphology for two different compositions was evaluated by TEM, and SAXS.

Conclusions

PHB/PCL 50/50 and 20/80 w/w and 5% MMT30B nanocomposite materials were obtained by twin screw extrusion, and films were prepared by cast film extrusion in pilot scale. The effect of MMT30B incorporation for two different blend compositions was studied by TEM and SAXS. In these films obtained by cast extrusion, clay acts as an emulsifier in the blend, localized at interface region and PHB phase preferentially, leading to a change in blend morphology. The incorporation of 5% of clay also modifies PHB crystalline structure.

TEM images PHB/PCL/MMT30B: left 50/50/0; right 50/50/5
Addressing The Challenges: Improving Polymer Characterization By Size Exclusion Chromatography

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Abstract

Synthetic polymers, as well as most natural polymers possess a distribution of molar masses. The ability to accurately and precisely characterize the molar mass distribution and averages is essential as the shape and the breadth of a polymer’s molar mass distribution will dictate the end-use properties of the polymer, such as hardness, tear strength, impact resistances, wear, etc. One of the most highly used tools for characterizing the molar mass of polymers is size exclusion chromatography (SEC). Here, we will show the multiple utilities of SEC along with the time and resource saving benefits of implementing a chromatography system with low dead volume, a dual-flow refractive index detector and semi-micro columns. We will demonstrate how single-detector SEC can be used to monitor the synthesis of PEGylated polymers and to determine the oligomeric content of a polymer. The dual-flow design of the RI detector in conjunction with semi-micro columns allowed for fast and accurate characterization of polymers intended for biological use. Additionally, we will show how SEC/RI can be used for quality control procedures. SEC/RI was used as an approach to failure analysis for automobile parts and the characterizations of commercial rubbers. The molar mass distributions of these synthetic polymers was fully characterized in less than 20 minutes and provided significant pictorial and numerical data for the differentiation between products. Finally, we will show how SEC coupled to a train of detection methods can be used to provide a detail picture of molar mass and polymeric size of natural polymers, such as sugar beet pectin. Through these multiple applications we will also demonstrate how a low dead volume SEC system equipped with a dual-flow refractive index detector and semi-micro columns will save time and resources when analyzing polymers.
Characterizing Copolymer Compositional Heterogeneity by GPC-FTIR Combined System

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Abstract

FTIR spectroscopy is a powerful technique for determining structural and compositional information of copolymers. Hyphenating gel permeation chromatography (GPC) with an FTIR detector through an automated solvent removing interface allows compositional and structural characterization across the whole molecular weight distribution of a complex copolymer. A GPC-IR hyphenated system was used to characterize various copolymer samples of SBR rubber, SEBS, Copovidone PVP/VA, PLGA and acrylate-styrene copolymers for compositional variations across MW distributions. Significant amounts of compositional drifts were observed for SBR, PVP/VA samples, whereas smaller levels of compositional drifts for SEBS and no compositional drifts were observed for PLGA copolymer. GPC-IR was also used to investigate a complicated copolymer system based on PMMA/BA (~6:1 ratio) main backbone but incorporated with small amounts of methacrylic acid, styrene and DAAM comonomers in order to improve various copolymer end-use properties. Different patterns of compositional heterogeneity of those copolymers with the 3-5 comonomers were found for a structure-property correlation study. GPC-IR hyphenated technology is well suited to characterize copolymer compositional drift across MWD, supplier-to-supplier / lot-to-lot variations and polymer compositional changes from a processing.
Development And Testing Of Innovative Hydrogels For Cultural Heritage Applications

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Abstract

In the field of cultural heritage hydrogels and high viscosity polymeric dispersion are used for cleaning and removal of superficial layers in artistic handiworks and for diagnostic purposes. Gels allow limitation of unwanted effect due to direct application of solvents, as swelling and extraction of original materials. Required features are the possibility of incorporating solvents and suitable viscoelastic properties to obtain workable shapes and complete removal after application.

A polymer chosen as gellant must be able to form gel by itself or with addition of a crosslinker. One or more additives can be added to obtain desired viscoelastic properties or to improve retention of cleaning solvents in the gels. The ratio between different formulation components can be varied to modulate gel properties.

Polyvinylalcohol (PVAI) in the presence of borax as crosslinker is known to form hydrogels capable of incorporating organic solvents. To improve mechanical properties and compatibility between gel and the co-solvent, formulations with different amounts of polyethyleneoxide (PEO) added to PVAI were investigated in this work. Transparent gels with interesting viscoelastic properties have been obtained and it was found that the addition of PEO increases the retention of water and of the organic solvent. Under conditions of practical applications these gels showed better performance than similar gels without PEO. The structure of the composite gels is under investigation in order to find correlations with their stability behavior and the physical properties.

Highly stable and clear gels have been also obtained by reaction of glutaraldehyde with the hydroxyl groups of PVAI under properly selected conditions. Different viscoelastic properties may be obtained, and the system appears apt to be modulated and to incorporate organic co-solvents and other additives suitable for conservation applications.
Multivariate Analysis Of THM-GC/MS Data For Classification Of Polysaccharide Binding Media

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Abstract

Plant gums are polysaccharide materials used in artistic field as binding media. The well-known method of Thermally Assisted Hydrolysis and Methylation (THM) was improved to be suitable for monosaccharide and polysaccharide identification [1]. The markers identified were attributed to the products of alkaline reaction of monosaccharides and can be useful for identification of carbohydrate materials. However these markers allow only a preliminary distinction between the different gums because they are not representative of the entire monosaccharides profile. Being impossible the classification on the basis of sugars quantification, multivariate data analysis was employed choosing as variables the peak area of monosaccharide markers.

In order to explore similarities and differences between plant gums and for identification of unknown gum in a real sample, several set of data were employed to obtain Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (CA) models. The aim of such data treatments is to discover clusters in a set of samples or objects on the basis of different data elaborations and create a reference model containing all the gums analyzed. Data set include gums artificially aged with termoxidation, fotoxidation, enzymatic treatment and ozonolysis. Some pigments were also added. Gums analysed were gum arabic, gum tragacanth, cherry gum, gum karaya and gum ghatti.

The survey of py-GC/MS data with Agglomerative Hierarchical Clustering and Principal Component Analysis offers a solution for deeper understanding of the gum differences and more detailed classification, while straigth analysis of pyrograms is not sufficient to obtain information about the type of gum. The reference model allows good gums identification and highlight some differences between aged and unaged materials. The PCA model derived from reference gum samples could be successfully applied to the identification of polysaccharide binding media in ancient samples collected from funerary Egyptian masks.

Chemical Identification Of Unknown Multilayers At The Nanoscale: AFM-Based IR Spectroscopy And Thermal Analysis

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Abstract

Using atomic force microscopy (AFM)-based nanoscale infrared (IR) spectroscopy and thermal analysis (TA), the cross-section of an intact multilayer polymer film with inclusions is chemically identified and linked to its AFM image. Since these techniques employ AFM tips with radii of tens of nanometer, the AFM-IR and AFM-TA measurements achieve 100-nm in spatial resolution. AFM-IR spectroscopy relies on detecting the local thermal expansion of the material upon absorbing 10 ns pulses of radiation from a tunable infrared source. Standard AFM tips are used to detect the ringing motions caused by the rapid heating and expansion of the sample. The amplitude of the ringing motion is proportional to the absorptivity of the sample, and hence the resulting AFM-IR spectra are similar to conventional infrared spectra. Nanoscale thermal analysis of the sample can be achieved by using a specialized probe that has a resistive heating element embedded at the tip. As the voltage applied to the tip increases, the material in contact with it would expand and the deflection of the AFM tip would increase until reaching its softening point. This is defined as the transition temperature and is correlated favorably with bulk thermal analytical techniques. The same nanoTA tips can also be used to map and measure the mechanical properties of the sample by using the Lorentz contact resonance mode. Since the abovementioned techniques do not require physically extracting each layer of the film, these localized analyses ensure the chemical integrity of the film as well as the exact arrangements of the components. Coupling the chemical, thermal and mechanical information from individual layers of the film, the exact composition can be readily identified.
Characterization Of Poly (2-Oxazolines) With MALDI-TOF Mass Spectrometry

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Abstract

Poly(2-oxazolines) present a diverse category of functional macromolecules, as their side chain can be tuned to easily provide water soluble and thermal-responsive materials. However, these compounds are notoriously difficult to synthesize as their cationic polymerization is sensitive to trace impurities that can lead to chain transfer byproducts. As a result, high molecular weight poly(oxazolines) (>60,000) are exceedingly difficult to prepare. Because end group fidelity is of critical importance in providing synthetic access to more complex architectures, e.g. block copolymers, methods for qualitatively and quantitatively determining end group functionalization are invaluable. Traditional characterization techniques employed by small-molecule chemists such as NMR spectroscopy, GPC, MS and IR do not afford sufficiently precise measure of end group functionalization, because the signal from the repeat units overwhelms those of the end groups. However, MALDI-TOF MS provides an exceptionally powerful tool for determining end group functionality and confirming end group transformations. In particular, end group modifications to incorporate “click” functionalities were explored, and their subsequent conjugation reactions.
Synthesis And Characterization Of Cyclic Triblock Copolymers Prepared Using “Click” Cyclization

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Abstract

Cyclic polymers have been the subject of increased research in the recent past owing to their unique physical and chemical properties and their distinct applications relative to their linear analogs. Some of the superior properties include enhanced stability and encapsulating capacity. Further, in the case of cyclic diblock copolymers with contrasting blocks (e.g. hydrophobic and hydrophilic) unique phase segregation in bulk and self-assembly in solution have been described. In order to probe the unique assembly behavior further, cyclic triblock copolymers have been prepared. Poly (ethylene glycol)-b-poly (e-caprolactone) diblock was synthesized using ring opening polymerization of caprolactone with a-hydroxy,?-azido poly(ethyleneglycol). The diblock was then coupled with polystyrene containing alkyne functionality using 1, 3-dipolar cyclo addition. Then the triblock polymer was reacted with sodium azide to yield a-hydroxy,?-azido triblock copolymer. Further, the triblock a-hydroxy functionality was converted to alkyne by using pentynoic anhydride to yield complementary functional groups (alkyne and azide) on opposite ends of each polymer chain. Cyclic triblock was synthesized by subjecting the polymer to 1, 3-dipolar cyclo addition using a slow, drop wise addition to ensure high dilution during the course of the cyclization. Owing to the contrasting physical properties of the different blocks, characterization of these compounds is particularly challenging. However, using a series of characterization techniques, including FTIR, NMR, GPC and MALDI-TOF MS, the structure and purity of these materials could be confirmed.
Synthesis Of Multi-Arm Cages Via “Click” Coupling

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Abstract

A variety of polymer architectures have been synthesized and investigated because of their strong correlation between nanoscale architecture to physical properties. So far, many researchers have developed a variety of synthetic tools to access a wide range of polymeric architectures and tailor the properties of macromolecules for their diverse application. Some of the few examples include hyperbranched perfluorinated/hydrophilic block copolymers for antifouling coatings, branched and dendritic structures for targeted drug delivery, globular polymers for the microelectronics industry, dendrimers for light harvesting applications, and polymer grafted scaffolds for catalysis. Synthetic routes for the preparation of various polymer architectures have long been a goal for polymer chemists, owing to their unique topology and physical properties.

Recently Laurent and Grayson reported an efficient method for synthesizing cyclic macromolecules using “click” chemistry which has proven to be a versatile way for making macrocycles. Also Tezuka reported the synthesis of multicyclic polymers by cyclization via ioinc pre-assembly followed by a covalent fixation. Further, the use of multicyclic “cryptands” demonstrated selective and strong interaction with potential guests. Inspired by these concepts, the synthesis of multicyclic “cage” polymers was explored. Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition fragmentation transfer polymerizations (RAFT) are powerful tools for preparing well defined polymeric architectures. ATRP is a particularly attractive approach for making star precursors because of the ability to modify the terminal end group in very high yields. The synthesis of polymer “cages” can be achieved by further clicking these end functionalized star polymers with a small molecule alkynylated caps consisting a complementary number of arms with respect to the polymer.
MALDI-TOF Characterization Of Linear Polymers Generated By Reversible Addition Fragmentation Chain Transfer (Raft) Polymerization.

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Abstract

The advent of modern controlled radical polymerization techniques has enabled the preparation of linear polymer chains with well-defined molecular weight and end group functionality. Mass spectrometry (MS) generally, and Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) MS specifically, has proven to be an invaluable tool because it allows for the unambiguous determination of polymer number average molecular weight (Mn), weight average molecular weight (Mw), and polydispersity (PDI) as well as providing reliable end group determination. In addition, this technique uses a negligible amount of sample, does not require the work-up of most polymer samples, and provides a relatively high throughput means of determining information about polymer distributions. Recently, Radical Addition Fragmentation chain Transfer (RAFT) polymerization has been used extensively because of its broad monomer compatibility for preparing polymers with tunable molecular weight and low PDIs. However, only limited work has focused on the MALDI-TOF MS characterization of polymer prepared using RAFT. Herein, the characterization of poly(methyl methacrylate) and poly(styrene), prepared via RAFT polymerization methods is explored, via MALDI-TOF, to determine the utility of this characterization technique for determining end group identity, and for confirming end group transformations.
MALDI-TOF MS Characterization And Monitoring Of Linear-Dendritic Hybrid Materials

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Abstract

MALDI-ToF MS was used to characterize well-defined hybrids consisting of linear poly(ethylene glycol) and dendritic polyesters because this technique provides tremendously detailed data to confirm the high structural purity of the dendronized PEG analogs. Characterization via MALDI-ToF MS at each step of the synthesis ensured that each step of the dendronization procedure was carried to completion. This is in contrast to methods such as NMR and GPC which, though useful for rudimentary product characterization, could not verify the overall structural purity. Because polymer purity is paramount for in vivo biomedical applications, MALDI-ToF MS represents a valuable technique for the detailed monitoring of these dendronization reactions and characterization of their products.
Mass Defect Tuned Dendritic Mass Spectroscopy Calibrants For Internal Calibration

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Abstract

Current mass spectrometry (MS) instruments, for example Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) MS require large macromolecules; such as dendrimers and well defined peptides, to calibrate their mass scale in order to provide highly accurate mass measurements. Polyester-based dendrimers are ideal for use as calibrants due to their rapid synthesis, high purity, wide molecular mass range and monodispersity. However, calibrants of this type contain predominately, H, C, O, N, and S, all of which display a positive mass defect. This positive mass defect can be particularly problematic when attempting to use them as internal mass calibrants for known compounds, because the analyte and calibration signal could become confused. The use of internal calibrants with polydisperse molecules, such as, synthetic polymers becomes especially tough in these conditions due to the multiple analyte signals over a diverse molecular weight ranges instead of being limited to a single mass. However, the use of tris-iodo dendritic calibrants results in a negative mass defect that distinguishes them from most common naturally occurring peptides and therefore allows for their use as internal calibrants. This is done by producing a molecule that is heavily weighted by the negative mass defect thus eliminating the likelihood of confusion of the calibrant and positively mass defect analyte signals. The mass defect offset of this technique can lead to a difference in signal mass peaks of nearly half a Dalton for typical “averagine” peptides with an identical nominal mass to that of the calibrant, allowing for the unambiguous assignments of calibrant and analyte peaks.
Field-Flow Fractionation for the Characterization of Rubber Polymers

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Abstract

Based on chromatography the field-flow fractionation (FFF) technology[1] has emerged to a unique and powerful method for analysis of particles, oligomers, polymers and even gel-like samples. By using a special separation channel without stationary phase common SEC-drawbacks resulting from phase interaction (sample degradation, filtration, clogging, abnormal elution) are generally overcome. The separation force applied (e.g. flow, thermal, centrifugal or gravitational) renders the FFF highly variable enabling the user to choose the most appropriate technique out of the FFF-family to obtain best performance.

In this poster, in particular the Asymmetrical Field-Flow Fractionation (AF4) is presented. To highlight its potential various rubber polymers including synthetic and natural samples were analyzed by AF4. Rubber is omnipresent in daily life ranging from "simple" household use to high-tech applications, like most prominent for tire production in the automotive industry. Since physical and mechanical properties are inherent polymer characteristics the natural polymer origin and changes within the formulation will influence the later application range. Therefore the determination of molecular weight, size and size distribution is important.[2]

# Latex Nanoparticle Analysis by Flow FFF-DLS Coupling

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## Abstract

Engineered nanoparticles (ENPs) are of widespread use for industry and increasing manufacturing, processing and utilization of ENPs lead to the presence of unnatural nanomaterial in consumables[^1–3] and the environment.[^4–6] The characterization of nanoparticles is of upmost interest with the need for straight-forward analysis technology. Since invention of the Field-Flow Fractionation (FFF) in 1966,[^7] FFF now has become a powerful separation tool based on chromatographic principles. Beside a fractionation range between 1kDa to 10^{12}kDa and a resulting high number of possible sample types, the FFF technology has become a powerful tool for the analysis of nanoparticles. The separation is achieved within flow streams in an unpacked channel. A force perpendicular to the sample stream line, like a second flow, thermal, centrifugal field or gravitation, is applied to facilitate separation. Thus, a whole FFF-family (platform) is generated according to the separation field applied, which enables the user to choose the most appropriate technique for a given task.

The poster presented here focuses on the analysis of latex nanoparticles by FFF, in particular by asymmetric Field-Flow Fractionation (AF4) coupled to a dynamic light scattering detector (DLS). By the combination of separation and analysis within one method one obtains detailed information about the size, size distribution and overall intensity of the sample (resp. correlation of size and an external input signal). Furthermore, the real-time analysis allows the user to directly monitor analysis progress and results during measurement. Thus, the coupling of DLS with AF4 facilitates a straightforward on-line size-analysis setup, which is exemplarily shown for latex nanoparticle standards. Any overestimation of hydrodynamic radii commonly accompanied by batch measurements (due to size averaging) can therefore be neglected and a time-resolved, true size-distribution is obtained.[^8]

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Polymer Analysis by Thermal Field-Flow Fractionation – PS, PMMA and PEO-PS

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Abstract

Field-Flow Fractionation (FFF), since invented in 1966,[1] has become a powerful separation tool based on chromatographic principles. With a fractionation range between 1kDa to 10^{12}kDa one can find various applications. Beside particles, especially polymers are accessible. FFF enables the user to analyze polymers comparable to common size exclusion chromatography (SEC) technology, but without having the disadvantages of sample shear degradation, clogging/altering of columns or phase interaction/adsorption effects. Truly advantageous of FFF are the utilization of a separation channel without any stationary phase inside and the possibility to choose from various subsystems within the FFF family. The unique FFF-techniques, all based on similar separation principles, allow the application of different separation forces, like thermal, gravitational or flow-streams in combination with appropriate detectors (RI, UV, LS, MS). Depending on the type of separation field used, these techniques are called Flow FFF (F4), sedimentation FFF (CF3) and thermal FFF (TF3).[2] However, besides the extended high molar mass region up to 10^{12}kDa compared to SEC, Thermal Field Flow Fractionation represents a highly valuable tool for the separation and analysis of polymers, polymer-blends, mixed or copolymeric samples.

In this poster the high separation potential of Thermal Field-Flow Fractionation (TF3) compared to common SEC analysis of different polymers is shown. Most prominent examples include the separation of polystyrene (PS), poly(methylmethacrylate) (PMMA), mixed polymer samples and blends thereof. The ability to separate by size and chemical composition[3] within one method, highlights the predominance of TF3 over standard SEC.

Opportunities For State-Of-The-Art Polymer Characterization At The Center For Nanophase Materials Sciences

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Abstract

The Macromolecular Nanomaterials group at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences, one of five DOE Nanoscale Science Research Centers, is the largest soft matter group at the laboratory. The group integrates polymer science with neutron sciences and theory/modeling/simulation. The suite of state-of-the-art polymer characterization tools within the CNMS are an integral part of the User Program. This poster will highlight the research capabilities of the Macromolecular Nanomaterials Group, as well as opportunities to work as a User at the CNMS.
Quantification Of Silanol End-Groups In Polydimethylsiloxane By GPC

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Abstract

Quantification of functional end-groups on polymer chains is important to study further reactions on those polymers. However, this is very challenging, especially for those functional groups which are difficult to be detected or derivatized. In this work, quantification of silanol end-groups on polydimethylsiloxane (PDMS) was studied. A novel and simple method was developed. This method used GPC-light scattering or universal calibration to get absolute molecular weight, and then calculated concentration of silanol groups by calculating the number of PDMS molecules. Small molecules will not interfere with the calculation as they were separated from polymers by GPC. The results agreed well with NMR. This method can be used for many other polymers in which the number of functional end-groups in each polymer chain is a constant.
Structure-Property Correlations Of 1-Butene/Ethylene Plastomers

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Abstract

Some samples of random copolymers consisting of 1-butene modified with a low ethylene content (4, 5, 8% by weight) produced with metallocene catalyst are characterized. The ethylene content in the copolymer C4C2 influences the physical properties of the final product, in fact increasing the content of C2 decreases the crystallization rate, the melting temperature and the crystallinity.

The crystalline form that is obtained from the melt depends on the experimental conditions (pressure, cooling rate, etc.), the molecular weight of the samples and the ethylene content. 1-butene copolymers with an ethylene content of less than 3% by weight crystallize from the melt in form I and form II; the fraction of form I increases with the C2 content.

The rate of the transition (solid-solid) from form II to form I is higher in presence of ethylene, on an equal molecular weight.

In the samples produced by metallocene catalyst, the decrease of the crystallinity and the melting temperature is faster compared to copolymers synthesized by Ziegler-Natta catalysts. Another peculiarity of these samples is that, when the ethylene content is higher than 3-4% by weight, they do not crystallize from the melt. The samples are in fact in the amorphous state just cooled down to room temperature. In the samples subjected to aging it is possible to observed the crystallization directly in form I (or I'), so there is no solid-solid transformation from form II to form I.

The structure of these materials have been studied by X-Ray diffraction (WAXD), nuclear magnetic resonance in the solid state (SS NMR), infrared spectroscopy (IR and ATR) and differential scanning calorimetry (DSC). The morphological study was carried out by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) and an excellent agreement was obtained in the results1,2.

The information obtained were correlated to the final properties of this new class of materials that combine high flexibility with good elasticity and very high ductility and can be processed directly or used as modifying agents in polymers.

References:
2) V.Causin, C.Marega, A.Marigo, G.Ferrara Polymer 46, 9533-9537 (2005)

SAXS patterns and trace calculated by fitting procedure and TEM image of sample PBET5
Hyphenated GPC/SEC With Electrospray Ionization Mass Spectrometry (ESI-MS) For The Determination Of Absolute Molar Mass Of Phenol Formaldehyde Resins

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Abstract

Phenol formaldehyde resins are formed by a step-growth polymerization. GPC/SEC with RI and UV detection is often used to characterize resins and to quantify the amount of different oligomeric species. Additional information is available if a ESI-MS-spectrometer is on-line attached to the GPC/SEC system. This technique combines the separation ability of GPC/SEC with the sensitivity and specificity of detection from MS and allows to identify oligomeric species and to learn about the degree of CH₂-OH substitution.
Size Exclusion Chromatography- Electrospray Ionization Mass Spectrometry (SEC/ESI-MS): Functional Polymer Characterization

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Abstract

In the current contribution we present novel developments in online size exclusion chromatography – electrospray ionization mass spectrometry (SEC/ESI-MS) of synthetic polymers. An emphasis will be made on the development of a software suite dedicated to the comprehensive analysis of synthetic polymers by SEC/ESI-MS (a collaboration between the Karlsruhe Institute of Technology (KIT) and PSS GmbH, Mainz). This software tool is aimed at providing non-expert users with automated means to perform spectral information processing of polymer mass spectra obtained from online SEC/ESI-MS. The peculiarities of spectra obtained using electrospray ionization, such as multiple charging and the mass bias on ionization in quantification are taken into account.
The Role Of Fumed Silica On The Morphology And Rheological Properties Of PET composites And PP/PET Blends

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Abstract

Polymer blending is a convenient route for the development of new polymeric materials, which combine excellent properties of more than one material. Additionally, many applications request the use of reinforced materials, and the development of composites has been widely studied with this purpose. Numerous researchers described polymer-clay nanocomposites based on single polymer matrix but a new approach in the nanocomposites studies consists in nanocomposites based on blends of two or more polymeric materials.

The present study investigates the effect of mixing fumed silica (SiO2) with Poly (ethylene terephthalate) (PET) and recycled PET (rPET) composites. Also blends of Polypropylene/Poly (ethylene terephthalate) containing fumed silica were prepared. In order to improve the compatibility in blends of PP/PET and PP/rPET maleic anhydride grafted polypropylene (PP-MA) was used. The samples were melt-compounded in a twin screw extruder. Differential Scanning Calorimetry (DSC), Atomic Force Microscope (AFM), Thermo Gravimetric Analysis (TGA) and Frequency Sweeps to obtain rheological data were performed. The effect of the addition of the PP-MA and fumed silica on the morphology and rheological properties was also evaluated.

Characterization of composites showed that there is no difference when using PET or rPET. Also the presence of the filler does not impact greatly the performance of the matrices by themselves. For blends of PP/PET-rPET the results show a better dispersion of the fumed silica when PP-MA was used. Due to the dispersion of filler in blends the crystallization and melting temperature was impacted and also degradation at higher temperatures than the pure matrices was observed.
Characterization Using EPDM Rubber As Filler Waste Vulcanized Rubber For Physical And Chemical Testing

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Abstract

A wide variety of rubber is produced to meet various industrial and domestic segments. These artifacts are produced from natural or synthetic rubbers. The improper disposal of these artifacts, post-use or post-processing for vulcanization, causes damage to the environment because these materials are not incorporated into the soil by decomposition in the short period. This study aimed to characterize compounds rubber EPDM (ethylene-propylene-diene), vulcanized with sulfur, and using the waste vulcanized rubber, observing possible changes in the mechanical and chemical properties. Three compositions were processed, without being a rubber waste, and two rubber waste in proportions of 5% and 10%. It was observed that there were no significant changes in the mechanical properties of hardness Shore A. The mechanical tests for tensile strength were carried out according to standard ASTM D 412. There was a decrease in property tensile at break, with increasing concentration of cargo. Relative to compound 1, without the addition of rubber waste, there was an increase in elongation for compound 2 (with 5% waste) and compound 3 (10% waste). It was also observed that there was a decrease in modulus of elasticity with increasing concentration of waste. Resistance tests were performed to fluids in accordance with SAE J 200 and ASTM D200. All samples tested at 125 °C for 70 hours showed the same variation Shore A hardness of 4 points; variation in the tensile stress of -5% (decrease) and changes in elongation of 35% (reduction). To test the oil resistance was used 15W40 oil at 100 °C for a period of 22 hours. After immersion oil for all samples, reduction in hardness, for compounds 2 and 3, relative to compound 1, a decrease in the breakdown voltage of approximately 16%. Were also performed, testing under the following conditions: 70 hours at 125 °C, and 72 hours in ethylene glycol, diluted in water at a ratio of 1 part to 1 part, at the temperature of 105 °C.
Applicability Of Rigid Hybrid-Based Packing Materials For Size-Based Separations Of Synthetic Polymers

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Waters Corporation, 34 Maple Street, 01757, Milford, MA, USA

Abstract

The technique of Gel Permeation Chromatography (GPC) was first described by J.C. Moore (J. Polymer Sci A, 2, 835, 1964) for the fractionation of synthetic polymers by molecular weight using crosslinked polystyrene gels in non-aqueous mobile phases. The separation mechanism for GPC is based on the size of the polymer in solution relative to the pore size distribution present in the column's packing material. This separation mode relies on the absence of all other separation mechanisms, such as hydrophobic interaction or ion-exchange.

Historically, packing materials for GPC have been exclusively organic polymers, such as hydrophobic crosslinked styrene-divinyl benzene gels or hydrophilic methacrylate gels. However, these gel columns do not provide the highest efficiency due to their lack of rigidity and susceptibility for compressing under pressure. The goal of this paper is to investigate the use of low dispersion chromatographic systems in combination with high efficiency essentially non-compressible hybrid packing materials. These hybrid materials have been synthesized to have pore sizes ranging from 50Å to 450Å, and were evaluated with regard to their ability to perform size-based separations. Initial evaluations were performed to determine the usable molecular weight range for each of the pore size materials and the results are compared to those of commercially available materials of similar pore size.
Polymer Analysis By Convergence Chromatography Using Sub-2um Particle Stationary Phases

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Abstract

Currently, analysis of synthetic polymers is performed to determine the molecular weight distribution and chemical composition as well as other material characteristics. Polymers are typically analysed by gas chromatography (GC) or liquid chromatography (LC). However, this analysis may be impacted by factors such as limited thermal stability as well as limited chromatographic resolution for the oligomers present in the polymer sample. Convergence chromatography provides analysts with an appealing alternative. Ability to use lower column temperatures than in GC, as well as the combined selectivity space of normal phase LC with reversed phase LC, offers the analyst another tool for difficult separations.

In the current study several polymers were separated using Acquity UPC2 system with sub-2 µm particle stationary phases. Preliminary results indicate that this analytical technique is applicable to polymers with average molecular weight up to 4000 Da. Example chromatogram of polystyrene with average molecular weight of 1300 Da is shown in Figure 1. Advantages include compatibility of convergence chromatography with either polar or non-polar solvents, reversed phase and normal phase columns.

Figure 1. Polystyrene (Peak MW=1300 Da). Acquity UPC2 system, Acquity HSS Cyano 1.8 µm, 3x100 mm column
Abstract

Nowadays, polymeric materials are inescapable in our modern societies and cover a broad range of applications in areas such as automobiles, textiles, packaging, medical and pharmaceutical, to name just a few. This increasing complexity in applications has driven the need to produce new, and often highly complex, polymeric materials. Accurate and detailed sample characterisation is vital to this process. It is predicted that the 3D structure of a polymer will have functional importance as synthetic polymers become increasingly sophisticated. Traditional techniques used by the polymer industry cannot measure 3D shape, which is greatly influenced by the flexibility of the polymer chain.

Travelling wave ion mobility separations coupled with quadrupole time-of-flight (QTof) mass spectrometry provide unique capabilities for 3D shape characterization.

Two co-polymers were prepared for analysis, a random and a block co-polymer containing poly ethylene glycol (PEG) and poly propylene glycol (PPG) repeat units. They were first dissolved in 50:50 acetonitrile:water before further dilution to produce two 10 ppm solutions of each sample.

The polylactide sample was first dissolved in acetonitrile before further dilution to produce a solution of 200 ppm polylactide and 20 ppm sodium iodide.

The samples were introduced to the ElectroSpray (ESI) source of a SYNAPT G2 HDMS instrument via direct infusion (Harvard syringe pump) at 10 µL/min. Ion mobility data were processed using MassLynx v4.1 and DriftScope v2.2.

DriftScope can be used to generate mobility plots that display mass to charge ratio on the x-axis, drift time on the y-axis, and ion intensity represented by color. If we observe a roughly straight, diagonal line in the mobility plots this tells us that as the polymer increases in mass there is a predictable relationship with its size. A bend, or a kink, in the ion series indicates that as the polymer increases in mass the 3D arrangement of the polymer chain changes and possibly folds back on itself.

Both co-polymer samples contained PEG and PPG repeat units and had an average molecular weight of approximately 2000 Da. For the block co-polymer, the area with the highest ion intensity runs roughly diagonally across the plot. This is in contrast to the random co-polymer where we see a greater number of bends, or kinks, in the ion series.

This means that we can draw some conclusions about the 3D structure and flexibility of the two polymers. The block co-polymer has the most linear relationship between mass and shape.

Recently, academic research has been carried out on polylactides to determine the degree of polymerization at which the folding occurs, for a given charge state. Calibrating the mobility cell with a known standard allows collision cross section areas to be calculated. This information can then be used to confirm calculated 3D structures for the polymer at various degrees of polymerization and charge state.
Using DLS Microrheology To Fully Characterize The Dynamic Spectrum And Viscoelastic Properties Of Macromolecules In Solution

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Abstract

The characterization of the complete viscoelastic spectrum for solutions of macromolecules, to provide information on the type and timescale of underlying macromolecular dynamics, poses measurement challenges. With macromolecular relaxation times in such systems typically being of the order of milliseconds, conventional mechanical rheometers are unable to access the high frequency (short timescale) data required due to inherent technique limitations. The application of microrheological techniques for understanding the rheology and dynamics of macromolecular solutions is rapidly evolving, with optical microrheology based on Dynamic Light Scattering (DLS) in particular having attributes that are appropriate for characterizing relatively low viscosity systems.

This study shows how the combined benefits of conventional macrorheology and DLS microrheology techniques significantly extend the accessible frequency range for measuring the viscoelastic spectrum of macromolecular solutions. Changes in macromolecular dynamics are highlighted with variation in molecular weight and solution concentration.
Characterization Of High Molar Mass SBR And PBR Rubbers By Various Separation Techniques - ASFFFF/MALS, SEC-UV/RI And HPLC

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Abstract

Synthetic rubbers such as polybutadiene (PBR) and styrene-butadiene copolymers (SBR) are widely used in industrial practice e.g. in the production of automobile tires. It is well known that the functional and processing properties of these materials are a function primarily of molar mass distribution, molar mass averages, branching degree and molecular architecture, chemical composition distribution, average content of bound styrene and microgel content. The following separation techniques were used for detailed analyses of PBR and SBR rubber samples: 1) Size exclusion chromatography with dual detection SEC-UV(PDA)/RI. Using this method standard molar mass distribution and molar mass averages were determined. Universal calibration based on polystyrene standards was utilized for results calculation. In addition, in the case of SBR rubbers the average chemical composition and dependence of chemical composition on molar mass was found. For polybutadienes we can also estimate the level of oxidative changes in the polymer. 2) Gradient HPLC using reverse stationary phase and tetrahydrofuran/acetonitrile mixture as a mobile phase. The method is based on the combination of precipitation-redissolution and partition chromatography on the reversed-phase C18 [1]. As separation is based on the content of bound styrene in macromolecule the chemical distribution could be estimated. 3) Asymmetrical flow field-flow fractionation with MALS detector AsFFFF/MALS [2 – 4]. The technique was used for determination of (true) molar mass distribution, molar mass averages and degree of branching of rubber samples. The measured results of molar mass averages were compared with those measured using size exclusion chromatography and advantages and disadvantages of both the methods were discussed. It was shown that the combination of all these three methods provides an enhanced adequate characterization of polybutadiene and styrene-butadiene rubbers. However, it should be noted that these techniques by themselves cannot provide full exhaustive information on the rubbers as it is in the case of 2D-LC techniques.

References
Original Mechanical Characterization Of Single Micrometric Vesicle By Atomic Force Microscopy

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Abstract

The study of soft particle deformation is of paramount importance for the advancement of fundamental colloidal science as well as its biomedical applications, particularly in drug delivery and cell mechanics. Recent developments of both theoretical modeling and experimental techniques have made it possible to measure the deformation behavior of a single micro-/nano-particle (e.g. polyelectrolyte capsules, cells…) under compressive deformation and, therefore, to characterize its mechanical and interfacial properties [1].

We have already shown that the interactions of lipid membranes with water-soluble polymers play a role on vesicles mechanical properties [2]. Since cell mechanical properties are of great importance in the first steps of biological processes, we have decided to further study the role of membrane coating by a polymer on GUVs deformation. We have used a zwitterionic fluid lipid (DOPC) and a positively-charged polyelectrolyte: the chitosan.
This work reports the first extensive characterization of a fluid lipid membrane using the compression between two planes of isolated Giant Unilamellar Vesicles (radius > 1 µm). Reproducible and reversible force-deformation curves for individual GUV are obtained and reveal a radius-dependency of the liposome force response. Effective bending and stretching moduli of lipidic membranes are then simultaneously determined using a simple elastic model [3] for bare and chitosan coated GUVs [2,4]. Our original analysis illustrates the influence of a charged macromolecule-lipid membrane interaction on its mechanical parameters, and highlights the marked sensitivity of this method to investigate soft objects.

References
Hyphenated Thermal Techniques For The Investigation Of Complex Polymeric Materials

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Abstract

Thermogravimetry is a widely used technique in polymer characterization, however, the information retrieved is sometimes only limited. If the evolved gases are transferred to an appropriate analyzer valuable information can be obtained and thus insights into polymer degradation or even polymer architecture can be obtained. We have used a TGA-FTIR-MS hyphenation to characterize different copolymers as well as complex composites and compared the results to those obtained by pyrolysis-GC/MS, another hyphenated thermal technique, which is one of the most powerful instruments for the analysis of complex polymers or polymermixtures.

Figure 1 shows the results obtained from a polymethylmethacrylte-co-styrene block copolymer. Whereas TGA shows a rather homogeneous thermal degradation, both FTIR and MS reveal that the methylmethacrylate block starts to degrade at a lower temperature and the styrene block is more thermally stable. The same polymer was analyzed by pyrolysis-GC/MS and it could be shown that the pyrolysis temperature has a big influence on the quantitative determination of the monomer ratio.

In conclusion we can say that our approach to characterize copolymers by hyphenated thermal techniques is very promising and we have already successfully utilized these instrumentations in the characterization of complex novel polymeric materials and composites.

Fig. 1. TGA-FTIR-MS analysis of methylmethacrytate-styrene-copolymer.
Characterization Of Acrylamide Resins Using Static And Dynamic Light Scattering

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Abstract

Our research involves characterizing various acrylamide samples using dynamic and static light scattering to determine persistence length and polydispersity. Dynamic and static light scattering devices calculated the molecular mass and molecular size which helped to figure out the persistence length and polydispersity. Astra program is used to calculate the data and graphs. The samples experimented are the samples used in paper coating. This experiment helped to identify which sample would perform better for drainage on paper machine and/or wet and dry strength improvement in sheet of paper.
Scanning Force Microscopy And Polarized Confocal- Raman Microscopy For In-Situ Characterization Of Uniaxially Stretched Ethylene Based Thermoplastic Elastomers

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Abstract

Polyethylene based elastomers are low crystalline materials which show interesting elastic mechanical behavior due to physical crosslinking. Nevertheless, the morphology of these polymers is still sparsely resolved. For a better understanding of the unique mechanical properties, microscopic changes in morphology and strain-induced variation in chain orientation of two polyethylenes with statistically distributed octene or butene side chains were monitored during uniaxial stretching using scanning force microscopy (SFM) and polarized Raman microscopy. For these purpose a stretching device has been developed and integrated in an existing SFM to visualize differences between an unstretched and stretched sample. Additionally, the set-up will be used to determine crystallinity and orientation of the samples before and after deformation via polarized Raman microscopy and polymer chain orientations were calculated for quantitative analysis. The correlation between the orientation, the arrangements of the amorphous and crystalline phases and the mechanical properties of the material at different elongation ratios allowed an interpretation of the macroscopic behavior on the microscopic scale.
Characterization Of Polyethylene Glycol End Group Modifications With MALDI-TOF Mass Spectrometry

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Abstract

The end groups of linear macromolecules play a critical role in the resulting physical properties of the polymer and can enable the construction of more complex polymer architectures. Because it is often challenging to isolate products from starting material or byproducts during macromolecular end group modifications, quantitatively functional group transformations are of particular value for polymer chemist. However, traditional characterization techniques such as nuclear magnetic resonance spectroscopy, infrared spectroscopy and gel permeation chromatography have severe limitations when determining end group transformations because any signal that results from the end groups tends to be overwhelmed by the larger signal from the backbone. The reaction conversion ratio is difficult to determine accurately, complicating further synthesis. This work explores the modification the various polyethylene glycol end groups by using high efficient reaction such as thiol-ene click and confirming the quantitatively conversion of macromolecular end groups by using MALDI-TOF mass spectrometry. The precision of this technique enables the unambiguous differentiation of primary amino groups and hydroxyl group, which differ by only 1 mass unit.
Synthesis And Characterization Of Mikto-Arm Star Polymers By Using Stepwise Click Reactions

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Abstract

Mikto-arm polymers are star polymers consisting of three or more arms with different chemical compositions attached to the same central core. Because of the forced connectivity of these polymers chains with contrasting physical properties, mikto-arm polymers exhibit unique properties including distinct self-assemble behavior in solution and phase segregation in bulk. As a result, the synthesis of mikto-arm polymers represents an important goal for polymer chemists, but is inherently challenging. One of the more attractive routes to preparing mikto-arm is by the attachment of well-defined, pre-formed linear polymer arms to the same central core. However, because this approach requires numerous synthetic steps, the individual coupling reactions must exhibit extremely high efficiency in order to afford the desired product in reasonable yields and high purity. The characterization of these materials can be equally challenging, as each arm exhibits different physical properties making their characterization by GPC vague, and analysis by other techniques such as MALDI-TOF MS difficult. Reported herein is a synthetic approach which involves the use of successive “click” coupling reactions to yield mikto-arm polymers of exceptional purity. GPC could be used to confirm the lack of byproducts from incomplete couplings, while MALDI-TOF MS enabled a reliable measurement of the absolute molecular weight throughout the synthesis.
Synthesis And Characterization Of “Perfect” Multi-Arm Polyethylene Glycols By Using Stepwise Click Reactions

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Abstract

Because the physical properties of macromolecules are inherently dependent on their structure and connectivity on the nanoscale, the controlled synthesis of polymer architectures has become a fundamental goal for polymer chemist. To address this need, a variety of techniques have been developed for the synthesis of polymer with different architecture such as linear polymers, star polymers, brush polymers, dendrimers, hyperbranched polymers, ladder polymers and cyclic polymers. Multi-arms polymer, which consist of multiple linear chains connected to a central core, have a unique set of properties (e.g. crystalline, mechanical, and viscoelastic properties,) when compared with their linear analogs due to their multi-arm structure, globular shape and multiplicity of end groups. However, the synthesis of multi-arms polymer with flexible number of arms and length of linear chain can be complicated, as divergent “core first” techniques (in which multiple polymer chains are grown simultaneously from a multifunctional core) have been shown in some cases to yield materials with incomplete numbers of arms and unequal relative lengths of arms. Critical analysis of the traditional divergent “core first” is complicated by the difficulty in determining what structural impurities may be present. In contrast, this approach investigates the stepwise addition of single arms onto a core, and therefore enables the preparation of star molecules with an exact number of arms, and an exact degree of polymerization for each arm. The polymer was characterized by MALDI-TOF mass spectrometry which confirmed the “perfect” structure of multi-arm polyethylene glycol.
Mid-infrared spectroscopy is a well-established analytical technique to characterize the chemical composition of polymers. Hyphenating size exclusion chromatography (SEC) with an FTIR detector through an automated solvent-removing interface allows compositional and structural characterization across the whole molecular weight distribution (MWD) of a copolymer or complex polymer mixture. The SEC-IR system removes the solvent and deposits the chromatographic eluents as a continuous track on an IR-transparent ZnSe disc. The built-in interferometer simultaneously captures a set of time-ordered transmission IR spectra from the solid-phase deposit. The software system controls the data collection and performs data processing e.g. visualizing IR spectra across each SEC peak and plotting IR band chromatograms related to polymer functional groups. The ratios of those IR band chromatograms can be used to calculate copolymer compositional drift across MWD. The snapshot IR spectra at each elution time may be used for an IR database search to identify the chemical compositions.

The SEC-IR system is compatible with all common chromatography solvents such as water, acetonitrile, methanol, THF, DMF, DMSO, HFIP, o-DCB and TCB. Like LC–MS, SEC–IR is limited to the use of volatile buffers. Unlike MS which looks at molecular fragments, IR looks at the vibrational resonances of molecular bonds. For large molecules such as copolymers, IR's ensemble-averaging of like bonds simplifies data interpretation. This makes SEC–IR a useful tool to determine copolymer compositional variations across the MWD. For a complex polymer mixture each component can be identified through an IR library match, or monitored for any compositional changes during a polymer modification reaction or degradation from a thermal processing or ageing study.

Analyzing Copolymer Compositional Drift: Copolymer compositional drift is a variation of the relative amounts of comonomers incorporated into the growing polymer chains during polymerization and is caused by monomer reactivity differences and/or monomer concentration variations in the reaction environment. The synthesis process must incorporate controls to either reduce composition drift, or to tailor it to a profile that yields desired end-use properties. Traditional techniques to analyze the composition drift are time-consuming and include preparative SEC, fraction collection and multiple sample preparations. SEC-IR provides a fast and single lab procedure in < 30 minutes to determine the composition drift. The author will discuss various compositional drift patterns from a set of styrene-butadiene copolymer samples analyzed by SEC-IR.

Deformation of Complex Polymer Mixtures: Deformation of a flexible conductive ink obtained from the semiconductor industry completely identified its polymer (polyester and polyurethane) and additive (a latent cross-linking agent) components including their supplier information. This case study will be discussed in detail to illustrate the SEC-IR capabilities to deformulate complex polymer mixtures for competitive analysis, IP protection and analytical trouble-shooting in polymer-related industries.

Characterizing Polymer Degradation: SEC-IR was also used to study the two different degradation pathways of a polymeric additive (hydrogenated styrene-butadiene copolymer) used in a motor oil formulation under an accelerated ageing test at 170°C. The high MW polymer additive eluted before its oligomeric degradants followed by the low MW base oil. With the ageing times increasing, more and more polymer additive broke down to low MW degradants via oxidative cleavage as evidenced by increased ether (1000-1200 cm⁻¹), oxirane (806 cm⁻¹) and carbonyl (1700-1750 cm⁻¹) functional groups in the degradants. The remaining polymeric additive was partially oxidized with the oxygen incorporation showing in the ether and oxirane regions, but avoided polymer chain cleavage as evidenced by a similar SEC elution time.
Vendor Exhibition Abstracts

Vendor Exhibition Schedule

Monday Lunch
ACQUITY Advanced Polymer Chromatography (APC), The Next Generation of SEC/GPC Analysis
Waters Corporation

Combined Analytical Techniques For Polymer QC
Malvern Instruments Inc.

Expanding Your Polymer Characterization SEC Knowledge: Column Selection and Coupling of Detection Methods
Tosoh Bioscience, LLC.

Tuesday Lunch
PSS Solutions For Macromolecular Characterization
Polymer Standards Services (PSS)

A Novel, Direct Coupling Of Simultaneous DSC/DTA-TGA (STA) And FTIR Called Perseus™
NETZSCH Instruments North America, LLC

Small Angle X-ray Scattering (SAXS)
Xenocs SA
Abstract

PSS is a global leader and innovator in the design and production of particles and packing materials for high performance GPC/SEC columns. We provide the widest range of highly characterized macromolecular standards for calibrating GPC systems. We synthesize a wide range of tailor made polymers. Our WinGPC software is the most comprehensive suite of programs for macromolecular characterization and analysis and includes instrument control for all major providers of GPC instrumentation. We have a modern and sophisticated range of SEC and SEC related instrumentation for macromolecular (synthetic and bio macromolecules) analysis, identification, characterization and deformulation regardless of the architecture, topology or composition of a macromolecule.

PSS has developed analytical methods, interface technology and instrument and analysis software for using hyphenated techniques such as;

- GPC-Multi-angle Light Scattering (MALS) - (molar mass and topology)
- GPC-Viscometry - (molar mass and topology)
- GPC-MS - (identification, end group analysis)
- 2D Chromatography (LAC-SEC or LCCC-SEC) for deformulation by chemistry and size
- 3D Chromatography (LAC-SEC-FT-IR) for deformulation by chemistry, size and identification
- GPC-IR/NMR (identification)

These techniques can be used not only to identify polymers but can support further kinetic or mechanistic studies of polymerization processes.
Abstract

Size exclusion chromatography (SEC/GPC) is used for the characterization of polymeric material, specifically their molecular weight distribution. Resolution of polymeric species requires long column lengths and banked column configurations, resulting in lengthy analytical test cycle times and associated consumption of costly and often hazardous solvents. Additionally, many test sets suffer from minimal replicate data points due to long analysis time resulting data with limited statistical weighting.

Taking advantage of the advances in chromatographic separations instrumentation and innovative robust column technology, the Waters ACQUITY APC System allows for improved resolution of polymer distributions with significantly shorter chromatographic run times and associated reduction in total analysis cycle time. Built on a holistic approach for instrument and column design, an unprecedented control of separation conditions required for polymer size based separation is achieved. The resulting ACQUITY APC system enables precise data generation for polymer characterization. Additionally, richer data sets with replicate analysis are easily obtained within minutes and not hours.
Abstract

The use of multiple optimized analytical technologies including Triple Detection GPC, Flow Injection Polymer Analysis, Automated Dilute Solution Viscosity and Rheological measurements can be combined to optimize the work flow in current Polymer Quality Control Laboratories. The fundamental principles of these measurements will be reviewed to give analysts a greater appreciation of how these techniques work together to potentially reduce laboratory work load while improving overall Quality Control.
A Novel, Direct Coupling Of Simultaneous DSC/DTA-TGA (STA) And FTIR Called Perseus™

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Abstract

The interpretation of thermogravimetric analysis (TGA) signal alone can be difficult. A solution to this problem is evolved gas analysis which involves coupling the thermal analyzer to a spectrophotometer. Up until now this coupling has been done using adapters and heated transfer lines. In the new Perseus™ STA 449 F1/F3 (DSC/DTA-TGA-FTIR), the short, heated coupling interface without any transfer line minimizes the risk of condensation, makes the system robust and reveals an excellent correlation of TGA and FTIR. This is made possible through the unmatched alliance between two successful instruments: the NETZSCH STA 449 F1/F3 Jupiter® and the ALPHA® FTIR spectrometer by Bruker Optics. The direct Perseus™ coupling is superior for highly condensable materials. Additionally, there is no need for liquid nitrogen cooling of the IR-detector, which makes it particularly well-suited for test runs with an autosampler (robot) or for measurements of longer duration. The compact, space-saving design is yet another useful feature for labs in which space is limited. In addition, the STA can be used as standalone unit, strengthening the versatility of the system. This unique, compact combination of two powerful instruments creates a single device capable of characterizing the thermal behavior of organics/polymers/biomass and also inorganics/ceramics/minerals, more clearly elucidating the chemistry behind the processes under investigation.

Perseus™ STA 449 F1/F3 – Simultaneous DSC/DTA-TGA- FTIR System
Expanding Your Polymer Characterization SEC Knowledge: Column Selection and Coupling of Detection Methods

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Abstract

The backbone of polymer characterization via size exclusion chromatography is the column selected to perform the separation; without the correct column the information obtained from various detection methods, e.g. refractive index, light scattering, etc., becomes obsolete. The selection of a suitable SEC column for polymer analysis can easily become a daunting task as hundreds to thousands of different columns are currently available. However, selecting the correct column is required as the molar mass averages typically obtained from SEC experiments rely heavily on the quality of separation being performed. Here, we will discuss the different criteria involved in selecting the best TSKgel® column for polymer analysis. The importance of selecting a column that is suitable for the polymer undergoing analysis will be shown through applications of natural and synthetic polymers via single- and multi-detector SEC using TSKgel columns and the EcoSEC® GPC System. Lastly, we will provide an overview of the physiochemical properties obtained from single- and multi-detector SEC when the correct column is chosen.
Abstract:

Xenocs, distributed in the US by Mosaic Distribution LLC, provides advanced solutions for nanomaterials studies such as the Xeuss system, a high performance modular SAXS/WAXS equipment. Xeuss integrates state of the art detectors and our high brilliance GeniX 3D source, coupled to our latest generation of scatterless collimation for maximized useful flux on the sample and ultimate set-up resolution.

Small Angle X-ray Scattering (SAXS) is proving to be a powerful technique for getting information related to the structure of nano-materials. The method requires little sample preparation, is non-destructive and in contrast to microscopy probes a volume of the sample thus giving a statistically meaningful result. When combined with Wide Angle X-ray Scattering (WAXS) one can also get information on crystalline structure.

Please join our lunchtime presentation to get a review of the considerable progress made in laboratory SAXS/WAXS instrumentation. Rapid measurements and high data quality opens the way towards dynamic measurements with parameters like temperature, humidity, flow, DSC, shear as well as high precision structure resolutions. We will present various results illustrating capabilities of our high performance Xeuss equipment for polymer structural characterization.
List of Attendees

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