



ASMS 2023 Houston

Evening Workshop of the Polymeric Materials Interest Group: “Hydrocarbon Polymers”

WORKSHOP REPORT

Date: Wednesday, June 7th, 2023

Chair: Thierry Fouquet (Bausch & Lomb, thierry.fouquet@bausch.com)

Co-Chair: Anthony Gies (Dow, apgies@dow.com)

Attendance: 55 attendees

The 2023 evening workshop of the “*Polymeric Materials*” interest group was dedicated to the analysis of hydrocarbon polymers, with two tutorial presentations, one open discussion, and several announcements. This year, we used the application “*Mentimeter*” for most of the slides to engage the audience fully and spice up a lively workshop. By joining the presentation via their mobile phones or laptop, the attendees were able to post comments and to ask questions in real time, to answer instant polls or questions asked by the presenters in their slides and view the results on the screen in a didactic and funny way. It also allowed the hosts to gather email addresses and suggestions for next year’s workshop.

The slides are available at the following link:

<https://www.mentimeter.com/app/presentation/alw8sb3v8j72ctgyq4pmt44z7vjwt1td/rtgsk62g1nm4>

Overview

- **Welcome and opening remarks**

Thierry Fouquet briefly discussed the interest group business, including the mailing list (127 active addresses in June 2023), the LinkedIn group (<https://www.linkedin.com/groups/4009861/>, 193 members in June 2023), the virtual informal meetings scheduled quarterly and some of the associated recorded videos available in the group’s YouTube channel (<https://www.youtube.com/@asmsinterestgrouppolymeric2555>, unlisted videos only). He also discussed the pending Sanibel/Asilomar polymer mass spectrometry-based proposal, as well as the potential for a combined submission with the Exposomics interest group.

- **Tutorial style presentations, Q/A and open discussion**

- Hydrocarbon polymers analyzed with three mass spectrometers and six ionization methods
Robert B. (Chip) Cody, JEOL USA, Inc.

Chip reported on the analysis of various hydrocarbon polymers (including polystyrene, polypropylenes, polyethylenes, polybutadiene, chloroprene, acrylonitrile butadiene styrene) using a variety of mass spectrometers and ion sources (including MALDI, EI, CI, FI, PI and DART). He emphasized on the need for combining these techniques - with “no single method ideal for all applications” - and on the importance of efficient data processing and graphical representation using Kendrick and Van Krevelen plots possibly generated by commercial, freeware and open-source programs.

- New Approaches for Examining Complex Polyolefin Mixtures
Anthony Gies, Dow Chemical

Tony presented two case studies on the use of three-dimensional (3D) visualization plots to help troubleshoot performance issues in complex polyolefin-based materials. In the first study, a combination of MALDI-MS, NMR, and 3D visualization plots were used to probe the reaction mechanisms of cationic Pd(II) α -diimine (CPD) catalyzed polyolefins. Highlights included the use of TEMPO radical trapping studies to demonstrate that the metal-organic insertion light initiated radical (MILRad) polymerization mechanism proceeds through both coordination-insertion and free radical processes, where reactivity can be selectively switched by an external blue light stimulus. During the detailed characterization of these complex mixtures, 3D visualization plots were used to gain insight into side reactions and the radical stabilization mechanisms of the MILRad process.

For the second case study, a combination of MALDI-MS, MS/MS fragmentation, and 3D visualization plots were used to examine the end groups and architectural distributions within a model but-3-en-1-yl(phenyl)phosphine (BPP) functionalized poly(ethylene-co-propylene) (EP, ethylene/propylene polyolefin), which had been synthesized using a dual-headed chain shuttling agent (DHCSA). Microstructure characterization was performed using CID fragmentation to gain insight into their chemical connectivity, end-groups, and incorporation of the DHCSA – as well as its most probable location within the polymer chains. The benefit of this combined analysis approach is the process modification feedback, which is vital to manufacturing the desired end product.

- Initially scheduled: Live demonstration of data processing using some of the data presented by the two speakers and freeware programs.

Thierry Fouquet, Bausch & Lomb

Several members of the interest group kindly shared data files from hydrocarbon polymers prior to the workshop to be used as examples for the session. Due to time constraints, this demonstration was postponed until the next virtual meeting of the “Polymeric Materials” interest group in July.

- **Additional presenter and open discussion:**

- The Amination of Poly(butadiene)

Scott M Grayson, Tulane University

Scott shared a few slides about the characterization of samples from Sabrina Scott and Prof. Laurel Schafer at University of British Columbia, to provide answers to the following questions and ask the attendees their opinion: Can we tell from MALDI-TOF MS how many monomers have reacted to form an aminated polymer? If more than two monomers are aminated, can we determine the length in between any two aminations. Are these random or block incorporation?

- **Final announcement:**

- Innovations in Materials Characterization Technology Summit (August 7-9, 2023, Carnegie Mellon University, PA)

Bryan Katzenmeyer, Waters

Bryan was proud to announce the holding of the “Innovations in Materials Characterization Technology Summit” in August 2023, for conference-style interactions and presentations with delegates from academia, government, and industry and tackling topics such as chromatography, MS, thermal analysis, rheology, NMR, modeling, synthesis and sustainability.

ADDITIONAL NOTES FOR THE ASMS COMMUNITY

- Thierry Fouquet will serve as chair until the next ASMS 2024. Anthony Gies will then serve as Chair in 2025-2026. The Interest Group will appoint a new Chair-elect during the evening workshop 2024 (Chair-elect 2025-2026, future Chair 2027-2028).
- The “Polymeric Materials” interest group is hosting virtual meetings on a quasi-quarter basis, very well received by the community as a way to keep in touch throughout the year without waiting for the next ASMS conference. Typical topics include recent research results or issues, articles recently published, overview of conferences, ...

These meetings are open to all and publicized via the interest group mailing list and LinkedIn group.

- September 20, 2022, 11:00 am – 12:00 pm EDT

Focus topic: Characterizing Macromolecules & Complex Mixtures via Unconventional Mass Spectrometry Techniques

Featured speaker: Addie Keating, PhD Candidate at the University of Akron

Summary: Complex macromolecules are often resistant to traditional ionization techniques, and thus, require creative approaches to obtain structural information. Applications of ambient ionization sources, ion mobility, and tandem mass spectrometry were discussed to determine size, structure, and formation of macromolecules and sample

mixtures. This talk began with a brief discussion on recent applications of an open-source, deconvolution method for quantifying multiply charged, aqueous polymers analyzed via direct injection ESI-MS, followed by an overview on the advancements made with poly(styrene sulfonate) (PSS) as a novel selective noncovalent adducting protein probe (SNAPP). The remaining time was spent discussing the analytical challenges of an understudied, diverse class of biomacromolecules — melanins, along with their synthetic nanoparticle counter parts, often referred to as poly(dopamine).

Video available on demand (YouTube channel, unlisted video)

- March 2, 2023, 11 am – 12:00 pm EST

Focus topic: Overview of the tenth International Symposium on the Separation and Characterization of Natural and Synthetic Macromolecules

Featured speakers: Laurence Charles and Isaure Sergent (Aix Marseille University, France)

Summary: Back from Amsterdam where the tenth International Symposium on the Separation and Characterization of Natural and Synthetic Macromolecules (SCM-10) took place from 1 to 3 February 2023, Laurence Charles and Isaure Sergent (Aix Marseille University, France) gave the Interest Group a taste of this congress (scheduled every other year), with an emphasis on the presentations dealing with mass spectrometry for synthetic polymers.

Video available on demand (YouTube channel, unlisted video)