

Synopsis of the 2004 ASMS Fall Workshop on Polymer Mass Spectrometry

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This year's fall workshop of the American Society for Mass Spectrometry, which was held in Baltimore, Maryland last December 9-10, discussed synthetic polymer mass spectrometry and was chaired by Robert P. Lattimer (Noveon, Inc., Cleveland, Ohio, USA) and Chrys Wesdemiotis (University of Akron, Department of Chemistry, Akron, Ohio, USA). The workshop was co-sponsored by the Polymers Division of the National Institute of Standards and Technology (NIST) and follows polymer mass spectrometry workshops held at NIST in 2002 [1] and 2003 [2]. The format of the 2004 workshop was tutorial. Review-and-outlook talks were given in four major areas of polymer mass spectrometry (MS): Chromatographic Separations and MS, MS of Complex Compositions, Analysis of Polymer Surfaces, and MS Characterization of Polymer Structures. Each of the four sessions featured two invited speakers and was followed by a wide-ranging and lively panel discussion on the current and future directions of that area of polymer mass spectrometry. The presentations of the eight invited speakers will be summarized here.

The first talk was given by Harald Pasch (Deutsches Kunststoff Institut, Darmstadt, Germany) on "HPLC-MALDI-TOF Mass Spectrometry for the Analysis of Complex Polymers." Dr. Pasch's central message was that polymer analysis cannot be performed by mass spectrometry alone but must be complemented by other techniques. He discussed the interplay between mass spectrometry and high-performance liquid chromatography (HPLC) (which separates on enthalpic differences) and size-exclusion chromatography (SEC) (which separates on entropic differences). The advantages of liquid chromatography under critical conditions (LCCC) (which separates polymer mixtures based on end-group functionality) were emphasized. Separations are needed to reduce the complexity of mass spectra, while the mass accuracy of MS is needed to calibrate the chromatography and help identify effluent components. Current work centers on coupling chromatography directly to matrix-assisted laser desorp-

tion/ionization time-of-flight (MALDI-TOF) mass spectrometry for rapid on-line separation and analysis.

Kim R. Williams (Colorado School of Mines, Department of Chemistry and Geochemistry, Golden, Colorado, USA) spoke next on "Thermal Field-Flow Fractionation: A Polymer Separation Technique for MALDI-TOF MS." After giving a tutorial on field-flow fractionation (FFF), Prof. Williams discussed three ways to apply the force field necessary to separate polymer molecules: inertial, fluid flow, and thermal gradient. Using thermal FFF she gave examples of the separation of a wide array of polymer samples including simple polystyrene homopolymer standards, natural rubber, polystyrene-polybutadiene-polytetrahydrofuran blends, and core-shell colloidal particles. Turning to the topic of coupling FFF to MALDI-TOF MS she discussed the use of mixed solvents to lower the working mass range of FFF (which generally performs better at high mass, typically greater than 100 ku) to overlap with the working mass range MALDI-TOF MS (typically used for polymers less than 100 ku). Once this had been accomplished a large number of possibilities opened up including applications of MALDI-TOF MS to calibrate FFF, and FFF separations of wide polydispersity polymers, polymer blends, copolymers, and core-shell polymer particles.

The second session on MS of Complex Compositions began with a talk by Hajime Ohtani (Nagoya University, Nagoya, Japan) entitled "Complex Compositions of Polymeric Materials Studied by Pyrolysis-GC/MS." The controlled pyrolysis of polymers in the mass spectrometer allows for the identification of the monomeric building blocks of complex macromolecules. By studying *n*-mers with *n* less than about four and separating them with gas chromatography the average tacticity of the polymer can be directly determined. The end groups can be identified in a similar fashion. Pyrolysis is especially important when the molecular mass of the polymer is so great that intact oligomers cannot be resolved by mass spectrometry. In this case breaking apart the polymer is the only way to resolve the end groups by MS. The degree of polymerization of high mass polymers can also be determined in this way by comparing the intensity of end-groups to that of main-chain monomers. Dr. Ohtani further described the application of pyrolysis to highly crosslinked polymers where placing intact molecules in the gas phase is impossible. In this case, gas chromatography mass spectrometry (GC-MS) allows for the determination of the degree of crosslinking by comparing the intensity ratio of cross-linked moieties vs. non-crosslinked moieties.

The second talk in this session was given by Concetto Puglisi (Institute of Chemistry and Technology of Poly-

mers, University of Catania, Catania, Italy) and entitled "MALDI-TOF Analysis of Complex Materials Formed in Melt-Mixing and in Degradation of Polymers." Dr. Puglisi's talk began with an introduction to copolymer statistics and the great complexity that can be created when multiple monomers are polymerized to high degrees of polymerization. The exponential increase in possible structures quickly overwhelms the resolution of the mass spectrometer and individual oligomers can no longer be identified. His first example entailed the melt-mixing of nylons with reactive internal or end functional groups. Upon high temperature mixing (e.g., as found in an extruder) the two homopolymers quickly become random copolymers making the analysis of the extrudate very difficult. However, pyrolysis mass spectrometry was able, by studying the small *n*-mers up to the hexamer, to determine the degree of randomness in the product copolymer as a function of time and temperature as well as to ascertain the chemical mechanism by which this exchange occurred. The final part of his talk dealt with the photodegradation of Nylon-6 and of the polyetherimide Ultem. By the clever interplay of MALDI-TOF MS, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and size-exclusion chromatography (SEC) the extent of reaction, as well as the chemical mechanisms for degradation, were fully explained. This was of great interest to nylon users attempting to understand the long term effects of their materials to environmental exposure.

The first session on the second day was on the topic of Analysis of Polymer Surfaces. Joseph A. Gardella, Jr. (State University of New York, Buffalo, New York, USA) gave the opening address entitled "Time of Flight SIMS and MALDI Studies of the Surface Chemistry of Polysiloxanes and Biodegradable Polyesters: Quantitation." Prof. Gardella gave the main advantages of secondary ion mass spectrometry (SIMS) as providing information on only the top-most few atomic layers, having a high sensitivity and thus able to detect species having a very low concentration, the ability to form images ("chemical maps"), and the fact that sample surface chemistry is preserved when SIMS is performed under "static" (low primary-ion dose) conditions. His work on SIMS has focused recently on quantitation of surface chemistry to understand bioadhesion and biodegradation. He demonstrated that by standard addition one could quantitatively determine the surface coverage of an impurity polydimethylsiloxane (PDMS) on a polymer poly (hydroxyl methacrylate) (polyHEMA) surface by SIMS, and the amount of an oligomer (PDMS) in a higher mass matrix polymethylmethacrylate (PMMA) by MALDI. These results demonstrated that MS can be used quantitatively if a standard addition calibration curve is first created. Examples of SIMS depth profiling were given including for polymer blends, for biodegradable polymeric material degradation kinetics (e.g., for absorbable sutures), and for drug release rates and mechanisms from a biodegradable

polyester. Prof. Gardella concluded with the observation that MS can be used for quantitative chemical analysis and that one of the biggest factors impeding this development is lack of automated software for peak detection and integration.

David M. Hercules (Vanderbilt University, Nashville, Tennessee, USA) gave the second talk in this session. His central message was that high-mass polymer fragments only come from the very top-most surface of the polymer, and that by using time-of-flight mass spectrometry to detect these high mass fragments extraordinary surface sensitivity may be achieved. These larger fragment ions range up to 5000 u and are distinguished from the smaller mass but higher abundance fragments below 500 u. The larger fragments typically contain multiple polymer repeat units and can be used to determine copolymer block length or polymer architecture. Prof. Hercules gave an example of SIMS on PDMS showing that for a series of samples there was an increased concentration of low mass cyclic oligomers as overall polymer molecular mass increased. This was followed by an example of PDMS segregation at the surface of polystyrene (PS). Scratching the surface of the sample to remove some of the PDMS revealed the PS signal. This indicated that the absence of a PS signal on the virgin surface was due to PDMS segregation and not to ion suppression of the PS by the PDMS. The final examples dealt with the analysis of polyurethanes. By selective chemical attack before MALDI analysis, Prof. Hercules showed how the "hard" and "soft" blocks could independently be analyzed for block length and overall copolymer composition, something that no other analytical technique can do.

The final session of the workshop was on the subject of determining polymer structure by mass spectrometry. The first speaker was Hans Joachim Räder (Max-Planck-Institut für Polymerforschung, Mainz, Germany). Dr. Räder began his talk with an atypical example of a macromolecule, in particular, giant polycyclic aromatic hydrocarbons (PAH). Many of the higher mass species (i.e., those greater than about 1000 u) are insoluble. In order to prepare MALDI samples Dr. Räder described how a "solventless preparation" method may be used. The PAH to be analyzed and the MALDI matrix are mechanically ground together. The resultant powder is pressed onto the MALDI target and the excess blown off with compressed air. This was found to get excellent high resolution results, such that defects resulting from the PAH synthesis could be accurately described. This in turn lead to the identification of the best chemical processes to create defect-free PAHs. He next discussed end-group determination for PS, polycarbonate (PC), and polyfluorene (PF) using post-source decay (PSD) methods. The final topic covered was the application of PSD to the determination of copolymer sequences, specifically to polypropylene oxide/polyethylene oxide block copolymers. Unresolved parent ions of two isobaric

oligomers could be analyzed by PSD of the entire peak to thereby obtain sequence information based on the decay components from the two oligomers. These experiments are difficult to perform because a suitable matrix and the correct laser settings must be found to gently fragment the polymer, that is, fragment it but not to such an extent that only small n-mers remain.

The second talk of the polymer structure session was given by William J. Simonsick, Jr. (DuPont Performance Coatings, Philadelphia, Pennsylvania, USA) and was entitled "Polymer Structure by Advanced Spectrometric Methods." Dr. Simonsick began his talk with a history of automotive coating development over the last century. One hundred years ago coatings were macromolecular lacquers with molecular mass between 500,000 u and 1,000,000 u. Such high masses were used to create durable coatings. Today the molecular mass is closer to 5000 u in order to reduce the volatile organic compounds (VOC) needed to carry the polymer. Reducing VOC is required to cut costs, decrease drying times, and to protect the environment. In order to make tough coatings from such (relatively) small macromolecules after application they must be reacted in place. In order to do so they are fabricated with reactive end groups. Dr. Simonsick went on to describe the Fourier transform mass spectrometry (FTMS) system that allows him to analyze uncured coatings by either MALDI or electrospray ionization (ESI) mass spectrometry. The ESI source can be fitted to a gel-permeation chromatograph (GPC) to separate the constituents before mass spectrometric analysis. He next described the study of telechelic polymer synthesis with this apparatus. Telechelic polymer synthesis ensures two functionalized end-groups per oligomer. With chromatographic separation before the mass spectrometer, and the MS/MS capabilities within the mass spectrometer, structural and chemical information of complex graft copolymers can be determined. Specifically, linear, cyclic, or hyperbranched oligomers that elute at the same time in GPC can easily be identified by mass spectrometry. Subsequently the MS can be used to calibrate the chromatography.

Several clear themes arose from this workshop:

- 1) Chromatographic separations assist mass spectrometry by reducing the complexity of the mass spectrum, and mass spectrometry calibrates chromatographic separations and helps identify effluent components.
- 2) Complex polymers need to be reduced to their constituent building blocks in order to understand issues of chemical composition and chain structure. Reduction to fundamental building blocks can be done by pyrolysis, by ion impact as in SIMS, by metastable decomposition as in PSD in MALDI-TOF mass spectrometry, by ex situ chemical means, or by MS/MS as in FTMS experiments. Complex polymers include copolymers, blends, branched polymers, cross linked coatings as well as many other examples.
- 3) Polymer mass spectrometry is ripe for advances in quantitation. By use of standard additions, comparison to standard materials, or isotope enrichment, quantitation can be achieved in many applications.
- 4) Software and rigorous numerical methods are needed for rapid and quantitative analysis of complex polymer mass spectra.
- 5) Separations must be linked to the mass spectrometer in order to increase sample throughput. Also, faster separation methods are needed to make best use of the rapid analysis time that is characteristic of mass spectrometry.
- 6) Each of the following two texts were cited by several speakers as useful reviews of the current state of the field: *Mass Spectrometry of Synthetic Polymers*, edited by G. Montaudo and R. P. Lattimer (CRC Press, Boca Raton, 2002), and *MALDI-TOF Mass Spectrometry of Synthetic Polymers*, written by H. Pasch and W. Schrepp (Springer-Verlag, Berlin, 2003).

References

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2. Wallace, W. E.; Guttman, C. M.; Wetzel, S. J.; Hanton, S. D. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 518–521.