Analytical and Statistical Approaches in the Characterization of Synthetic Polymers

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Summary

Polymers are large molecules composed of repeating units called monomers. Polymers vary in terms of the monomer/s used; the number, distribution and type of linkage of monomers per molecule; and the side chains and end groups attached. Given this diversity, traditional single-technique approaches to characterization often give limited and inadequate information about a given polymer. Multi-technique but polymer-specific approach was found to be an appropriate alternative. This strategy was applied in characterizing polymers of a wide range of properties from simple polyethylene gylcol, to polycationic chitosan and aminopropyl based oligosiloxanes, and to polydiverse polyfluorinated polyethoxylates.

The molecular weight distribution of polycationic chitosan oligosaccharide was studied using size-exclusion chromatography (SEC) and mass spectrometry. The average molecular weights obtained by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) and electrospray mass spectrometry (ESI-MS) were significantly different from those obtained by SEC with poly(2-vinyl pyridine) molecular weight standards.

The polycationic nature of chitosan depends on the degree of deacetylation (DD). This single most important property dictates the behaviour of chitosans in aqueous solutions. Partial least squares (PLS) chemometric technique was successfully applied to improve the determination of DD using infrared spectroscopy. The values obtained for chitosan samples with unknown DD using IR-PLS were comparable to the values obtained by standard potentiometric titrations. In a separate study, the combined effects of DD and degree of polymerization (DP) on the ability of chitosan to bind with oil, was elucidated. PLS was used to correlate the oil-binding activity to DD and DP.

Siloxane-based and silsesquioxane-based polymers have been difficult to analyze using traditional techniques. Liquid chromatography with electrospray ionization mass spectrometry (LC-ESI-MS) was effectively utilized to determine the molecular weight distribution of in-house synthesized 3-aminopropyl oligosilsesquioxane. Single homologue siloxane standards were prepared by fractionating the sample in an octadecyl column by ion pair chromatography. The molar concentration of siloxane homologues in each collected fraction was assigned using induced coupled plasma – optical emission spectroscopy (ICP-OES).

Polyfluorinated polymers represent a contemporary class of materials with unique properties. One important group comprises of random copolymers of fluorinated ether monomers (methoxy, ethoxy and propoxy). High resolution mass spectrometry techniques like linear quadrupole – time of flight and orbitrap coupled to electrospray ionization were used to

determine the molecular formulas of the different species present in an unknown formulation composed mainly of polyfluorinated polyethoxylate. Separation in a C18 column and analysis of retention times gave additional insights as to the monomer composition of the polymer. The use of Kendrick's plot highlights the different ways in which the different species in the polymer formulation vary.

The research works included in this thesis have demonstrated that polymer characterization can be accomplished with the use of a combination of different instrumental and statistical techniques. This strategy allows the researcher to explore additional information about the polymer formulation and correlate these to some observed behaviors or activities.