Electrospray FTMS and MALDI TOF MS Characterization of $[(O_{3/2}SiMe)_x(OSi(OH)Me)_y(OSiMe_2)_z]$ Silsesquioxane Resin.

Ron E. Tecklenburg[1], Huiping Chen[1] and William Wallace[2]

1 Dow Corning Corporation, Analytical Sciences Department, Midland, MI 48686
2 Polymers Division, NIST, Gaithersburg, Maryland

Silsesquioxanes or three-dimensional organosilicon resins, have a long history in the material science community and continue to generate much interest due to their unique structures and physical properties. One particular structure type, methyl silsesquioxane nanotubes, are similar to carbon based fullerenes and carbon nanotubes except that these silsesquioxane based resins form at room temperature by simple acid catalyzed hydrolysis and condensation chemistries. The application areas for silicone resins range from i) coatings to insulate from heat, abrasion or electricity, ii) processing aids or modifiers for organic polymers, iii) interlayer dielectrics and iv) precursors to crystalline silicon carbide ceramics. While silsesquioxane resins have been commercially successful, very little detail exists about their molecular structure due to the extremely complex nature of the individual molecules present, which comprise the resin. Literally hundreds of individual structures exists in many silsesquioxane resins and many of these species cannot be resolved nor identified without the use of high mass analyzers and high resolution mass spectrometry techniques. The $(O_{3/2}SiMe)_x(OSi(OH)Me)_y(OSiMe_2)_z$ silsesquioxane resin is synthesized by the reaction of $MeSiCl_3$ and Me_2SiCl_2 at an 85:15 molar ratio in methylisobutylketone. This resin was fractionated by supercritical fluid extraction into 21 distinct fractions with narrower polydispersities, thereby making them much more ammeable to MALDI TOF MS analysis than the bulk resin itself. The extensive FTMS and MALDI TOF MS characterization data for this silsesquioxane resin is the subject of this presentation.

The OSi(OH)Me groups present in some of the resin molecules arise as uncondensed groups and therefore can lead to the observation of a slow increase in molecular weight and can give rise to long-term resin stability issues. The lower mass ESI FTMS data (500- 2000 Da) has allowed identification of the composition of resin species even in cases were isobaric resin species exist. Mass resolving powers up to 100,000 were required in some cases to baseline resolve resin ions of very similar *m/z*. For any given resin species with more than 7 silicon atoms, two or more possible structures can be drawn. Many of these structures are postulated to consist of partially open cages consisting of three, four and five membered rings comprising the faces of the cage structures. The average composition for the low molecular weight portion of the resin was calculated from the ESI FTMS data to be $(O_{3/2}SiMe)_{0.72}(OSi(OH)Me)_{0.13}(OSiMe_2)_{0.15}$. During the initial stages of hydrolytic condensation, resin species with 7 to 12 silicon atoms are produced. Many of these molecules were found to contain either zero or one OH group, thus suggesting that first generation resin species with more than one OH group react quickly to form second generation resin molecules with 12 through 20 silicon atoms per molecule. MALDI TOF

MS analysis of the high molecular weight portions of the resin detected molecular weights as large as 125 kDa.