

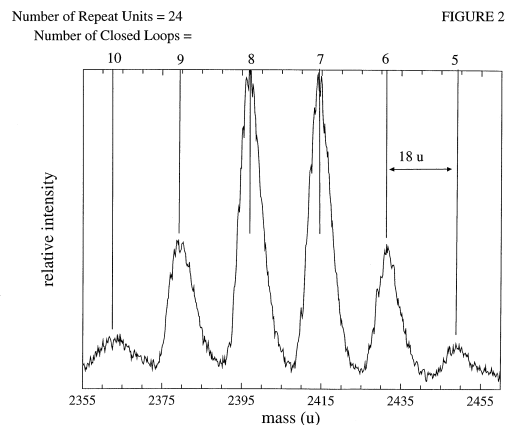
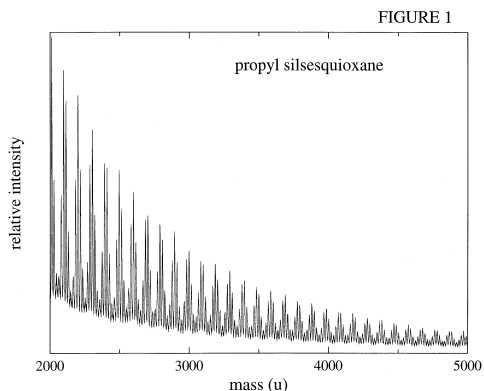
Polymeric Silsesquioxanes: Measuring the Degree of Intramolecular Condensation

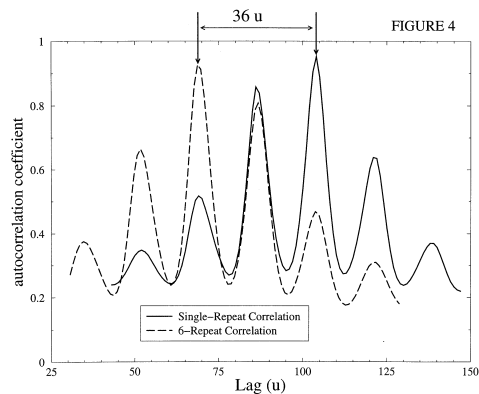
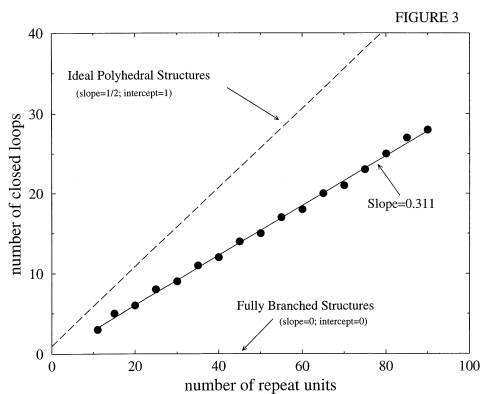
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Polymeric silsesquioxanes are increasingly being used as an alternative to siloxanes in applications where a highly-crosslinked final product is required. The silsesquioxane monomer is of the general form $\text{RSi}(\text{OH})_3$ where R is an organic substituent group. This leads to a final material that is an organic/inorganic hybrid with the chemical formula $\text{RSiO}_{3/2}$. Upon polymerization, some, but not all, of the -OH groups react with one another to form Si-O-Si bridges and water. Being trifunctional, the silsesquioxane monomer can form a host of complex three-dimensional oligomers including fully-condensed polyhedral structures (where all the -OH groups condense), ladder structures (where many of the -OH groups condense to form closed rings), and branched, linear structures (where no closed rings are formed). The formation conditions and resulting effects of these structures on processing and final properties are not well understood. This is largely due to the lack of an analytical technique to differentiate among these molecular structures. We have performed MALDI-TOF mass spectrometry on a wide variety of polysilsesquioxanes and have been able to make statements regarding the molecular structure of a given molecule [1,2]. In particular, accurate mass spectrometry has allowed us to count the number of residual -OH groups as a function of molecular mass and, therefore, to count the number closed rings per molecule thus quantifying the relative amounts of those that are polyhedral from those that are highly branched in a given sample.

The MALDI-TOF mass spectrometry was performed using sinapinic acid as the matrix with chloroform as the solvent. Cationization occurred due to adventitious sodium. The mass fraction ratio of matrix to analyte used was in the range of 10:1 to 5:1. The targets were prepared by electrospraying the analyte+matrix solution onto stainless steel target plates at a potential of 5 kV. This resulted in uniform target spots giving good signal at all locations on the plate. The instrument was used in reflectron mode with delayed extraction at an extraction potential of 25 kV.

FIGURE 1 shows the center portion of a mass spectrum for a typical hydrolysis-condensation silsesquioxane (here R=propyl). The exponential decrease in number of





ions as a function of mass is typical for condensation polymers. (Matrix-signal blanking techniques were used to ensure that this was not an artifact of detector saturation.) The estimated relative standard uncertainty ranges from 3 for the major peaks to 0.5 for the minor peaks of interest. FIGURE 2 shows the region around one oligomer of the polymer (where an oligomer is defined as having a given number of silicon atoms, n). Each group of peaks is separated by 18 u indicating a loss of one water molecule per oligomer as one moves to the left on the spectrum. For each loss of water a closed ring is formed intramolecularly. FIGURE 3 is a plot of the most probable number of closed loops in a given oligomer (equal to the number of lost water molecules, t) versus the number of repeat units in the molecule (equivalent to the number of silicon atoms in the molecule, n). The most probable number of closed loops is simply the highest peak for a given oligomer as shown in Figure 2. The estimated standard uncertainty for the number of closed loops in Figure 3 is one loop, t . The dashed line in Figure 3 has a slope of $\frac{1}{2}$ and indicates where the points would lie if the analyte consisted of fully-condensed polyhedra. If the structure were highly branched with no closed loops these points would lie on the abscissa (which is a line having a slope of zero). Instead the points lie in between, with a slope of 0.311 ± 0.004 (standard deviation), indicating a mixed structure having some closed loops but also retaining a large number of silanol groups. This slope is the key to determining the topological nature of the analyte. Instead of calculating by hand the most likely number of closed loops on an oligomer-by-oligomer basis (as done for Figure 3) the concept of the autocorrelation can be used to arrive at this result much more quickly. FIGURE 4 shows the autocorrelation of the data in Figure 1 for the region around 104.1811 u (the mass of one repeat unit) as a solid line and for the region around 625.0866 u (6×104.1811 u) as a dashed line shifted by $\Delta n=5$ so that they overlay. We see that the addition of 5 repeat units increases the number of closed loops by two (as indicated by the arrows in Figure 4). The ratio 2/5 (or 0.4) gives the slope of the line in Figure 3. In this case the value is overestimated (compared to 0.311). The source of this overestimation comes from using the highest peak for each oligomer instead of fitting the oligomer maximum intensities to a Gaussian function to find the true center of each oligomer's distribution. When this is done the resulting value for the slope from the autocorrelation analysis is 0.280 which is closer to the value derived by hand.

[1] W.E. Wallace, C.M. Guttman, J.M. Antonucci, *J. Am. Soc. Mass. Spec.* **10**(1999)224

[2] W.E. Wallace, C.M. Guttman, J.M. Antonucci, *Polymer* (in press)

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