

MALDI-TOF MASS SPECTROMETRY OF POLYMERIC SILSESQUIOXANES

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Introduction

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 $\text{RSi}(\text{OR}')_3$ where R is an organic substituent group, and R' is an organic leaving group. In the first synthesis step, this leaving group is hydrolyzed to form a monomer of the form $\text{RSi}(\text{OH})_3$. Upon polymerization, some, but not all, of the -OH groups react with one another to form Si-O-Si bridges and water. This leads to a final material that is an organic/inorganic hybrid oligomer with the chemical formula $(\text{RSiO}_{3/2})_n$. Being trifunctional, the silsesquioxane monomer can form a host of complex three-dimensional oligomers including fully-condensed polyhedral structures, e.g., cubes, (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 reaction parameters for the formation of the various structural types and the effects of these different structural variants 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 and those that are highly branched in a given sample.

Experimental

Polymeric silsesquioxane synthesis, which has been described in full elsewhere [3], was conducted in glass by combining the silsesquioxane monomer (either 3-methacryloxypropyltrimethoxy silane or 3-methacryloxypropyltriacetoxysilane), distilled water, acetone, and catalytic amounts of formic acid. The cloudy mixture was magnetically stirred at 23 °C until clear (≈ 30 min) and then heated at 65 °C for 4 d to remove acetone, water and other volatile by products to give a clear, slightly pink, viscous liquid. Thus, the same siloxane monomer with two different R' leaving groups, acetic acid and methanol, were employed in the synthesis under identical conditions.

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 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.

Results and Discussion

Figure 1 shows the center portion of a mass spectrum for a typical hydrolysis-condensation silsesquioxane (here R=propyl methacrylate). 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, defined as the signal-to-noise ratio divided by four, 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). In the case shown $n=10$. 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. This is indicated at the top of the figure where t , the number of closed loops corresponding to each peak, is shown. 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) for two different leaving groups (R'): methanol and acetic acid. 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. An error bar demonstrating this uncertainty is shown in the figure. The dashed line in Figure 3 has a slope of $1/2$ and indicates where the points would lie if the analyte consisted of fully-condensed polyhedra (e.g., cubes for $n=8$). If the structure were highly branched with no closed loops ($t=0$ for each n) these points would lie on the abscissa (which is a line having a slope of zero). Instead the points lie in between 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.

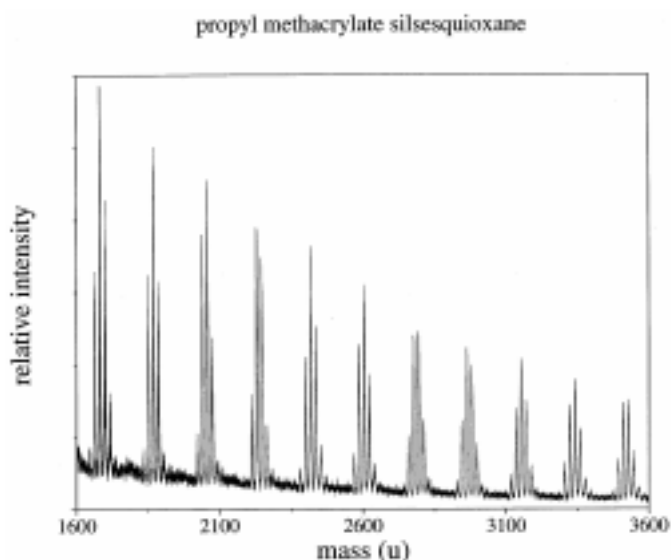


Figure 1. The central portion of the full mass spectrum of propyl methacrylate silsesquioxane showing the characteristic shape of a condensation polymer. Estimated standard uncertainty of the peak position from calibration and repeatability studies is 0.2 u, and the estimated relative standard uncertainty in overall signal intensity from repeatability studies is 15 %.

As for the two R' groups considered: acetic acid is known to have a substantially faster hydrolysis rate than methanol under the polymerization conditions used. This manifests itself in two ways. First, the degree of intramolecular condensation is greater for the acetic acid leaving group, i.e. its t vs. n line has a greater slope. Second, the overall degree of polymerization obtained for the acetic acid leaving group was greater than that for methanol, i.e. oligomers are observed to a higher value of n as seen in Figure 3. These observations can be understood by comparing the hydrolysis rate to the condensation rate. When the first is high compared to the second few opportunities to condense are lost because every site is reactive. When the condensation rate is higher than the hydrolysis rate then steric hindrance can work to slow down further hydrolysis (by excluding water from the R' group) or can work to retard condensation (by allowing the growing molecule to form conformations where further reaction is forbidden by bond angle effects).

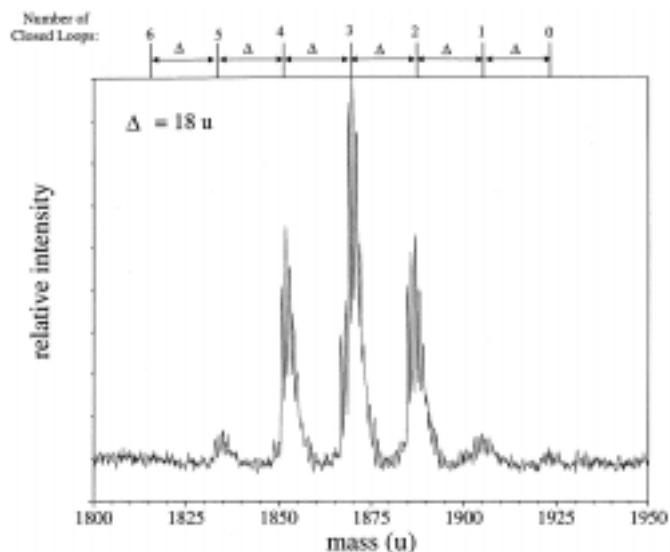


Figure 2. A single-repeat-unit detail of the full mass spectrum shown in Figure 1. The distance between peaks in this single major cluster is 18 u indicative of the intramolecular loss of water. These shifts of 18 u are shown at the top along with the number of closed loops t per oligomer.

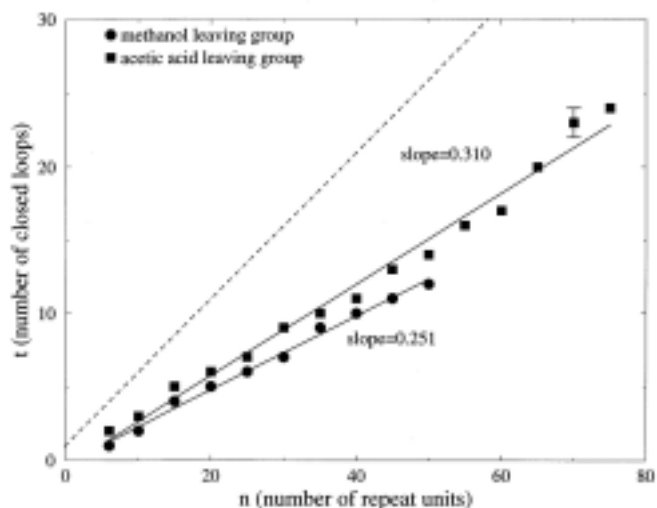


Figure 3. A plot of t vs. n for the two different leaving groups considered in this work. Uncertainty of ± 1 for t , as shown in the upper right, applies to each point on the graph.

Conclusions

MALDI-TOF mass spectrometry has been shown to be an effective method to determine the degree-of-intramolecular-condensation of polymeric silsesquioxanes. The nature of the organic R' leaving group was found to have a significant effect on the degree-of-intramolecular-condensation. Differences in the hydrolysis rates of the two R' groups provided a likely explanation for the effects observed. Broadly considered, these results point to a means to understand reactivity and gelation in silsesquioxanes and in condensation-reaction systems in general.

References

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