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Polymeric silsesquioxanes: degree-of-intramolecular-condensation measured by mass spectrometry

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Abstract

The degree-of-intramolecular-condensation, defined as the number of residual silanol (Si–OH) groups per oligomer, for a variety of silsesquioxane polymers was measured by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Condensation of the Si–OH groups of a given silsesquioxane oligomer leads to the formation of intramolecular Si–O–Si bridges accompanied by the loss of water. This elimination reaction is easily identified via high resolution time-of-flight mass spectrometry. Various polymeric silsesquioxanes were prepared from the corresponding trialkoxyorganosilanes by hydrolysis–condensation reactions at moderate temperatures (25–65°C) in aqueous acetone with catalytic amounts of formic acid. An *n*-decyl-silsesquioxane was found to have the highest degree-of-intramolecular-condensation with lower degrees found in *n*-propyl and in 3-methacryloxypropyl silsesquioxanes. An *n*-propyl silsesquioxane synthesized without a catalyst was found to have the lowest degree-of-intramolecular-condensation of all as well as the lowest overall molecular mass. In all cases the number of intramolecular Si–O–Si bridges per oligomer was found to be a linear function of the number of repeat units in the oligomer. This linear relationship is discussed in light of theories of intramolecular interactions and bonding in isolated chains. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Mass spectrometry; Silsesquioxane; Condensation polymerization

1. Introduction

Silsesquioxanes are increasingly being considered as an alternative to siloxanes in applications where high strength, thermal stability, or chemical resistance are a premium [1,2]. Siloxanes are linear polymers with a repeat unit of the form [R_2SiO] with each silicon atom coordinated to two bridging oxygen atoms. In contrast, silsesquioxanes with a repeat unit of the form [$RSiO_{3/2}$] can be made into truly three-dimensional polymers. In silsesquioxanes, each silicon is coordinated with three oxygen atoms. This three-fold coordination is closer to the four-fold coordination found in silica [SiO_2]. Ultimately, four-fold coordination is necessary to meet the strength and stability requirements. Silsesquioxanes are typically processed in two steps. The first is a hydrolysis–condensation sol–gel type synthesis [3,4] resulting in a low molecular mass prepolymer. It is this prepolymer that is studied here. The second step involves subsequent processing into final form to produce a fully crosslinked material with a four-fold coordinate structure. This final crosslinking reaction includes the condensation of residual unreacted Si–OH groups, and may include the hydrolysis or oxidation of the SiR to form a final Si–O–Si covalent bond (or "bridge") resulting in nearly pure silica; alternatively the functionalized R groups can react, for example by forming R–R or R–X–R covalent bonds, where X is a crosslinking agent. Unlike silica, the polymeric silsesquioxanes can be processed at low temperature, either neat or in solution. Unlike conventional siloxanes, polymeric silsesquioxanes are inherently functionalized and, thus, can be designed to be heavily crosslinked.

One important unknown that controls much of the processing behavior of silsesquioxanes is the "degree-of-intramolecular-condensation" of the polymer before it is converted into the final monolith. Degree-of-intramolecular-condensation is a measure of how many of the silicon atoms exist three-fold coordination with bridging oxygen atoms as opposed to how many have unreacted silanol (Si–OH) groups. The polymerization process to create the polymer is a condensation reaction of two silanol groups (or a silanol group with a silanol derivative) to create one Si–O–Si bridge with the elimination of water (or other small molecule

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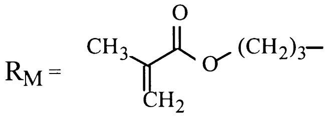

$R_P = CH_3(CH_2)_2$-

$R_D = CH_3(CH_2)_9$-

Fig. 1. The generalized structures of the functional R groups on the trialkyloxyorganosilanes used in this study. R_M is the structure of the 3-methacryloxypropyltrimethoxysilane (MPTMS) functional group, R_P is the *n*-propyltrimethoxysilane (PTMS) functional group, and R_D is the *n*-decyltriethoxysilane (DTES) functional group.

such as methanol). For the simplest case the reaction can be written as:

$$\text{Si–OH} + \text{Si–OH} = \text{Si–O–Si} + H_2O. \quad (1)$$

This process is expected to create linear or branched chains where there are $n + 2$ unreacted Si–OH groups on the chain or chains with internal rings resulting from intermolecular condensation reactions. Both the synthesis conditions and the nature of the organic R-group can affect the extent of polymerization, i.e. complete condensation typically does not occur. Instead, unreacted silanol groups are left behind. These unreacted silanol groups not only control the reactivity of the polymer in subsequent processing steps, but also control the three-dimensional molecular shape of the polymer which can influence such properties as solubility and solution viscosity. Until now the number of unreacted silanol groups has most often been measured by infrared spectroscopy. However, infrared only gives an average measure of the number of residual silanol groups in the polymer without regard to molecular mass dependence. Here matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry is used to quantitatively determine the specific number of silanol groups (and thus, the number of closed ring structures in each chain) as a function of the number of repeat units in the molecule. For any number n of silicon repeat units in the chain the fraction of chains with t closed rings can be determined quantitatively. This measure of the degree-of-intramolecular-condensation has been demonstrated on several types of R-substituted silsesquioxanes prepared under similar reaction conditions, and, in the case of an *n*-propyl silsesquioxane under two different synthesis conditions. Differences in the degree-of-intramolecular-condensation were found to be substantial. However, in all cases the number of intramolecular Si–O–Si bridges per oligomer was found to be a linear function of the number of repeat units in the oligomer.

2. Experimental

The generalized structures of the functional R groups on the trialkyloxyorganosilanes used in this study are given in Fig. 1. The synthesis conditions were chosen specifically to prevent either particulate precipitation or gelation of the product material. When either of those events occur the molecular mass of the products may become so great that mass spectrometry cannot be performed on intact molecules.

2.1. Materials

All reagents were used without further purification. Aqueous formic acid (mass fraction of acid, 96%) and 3-methacryloxypropyltrimethoxysilane (MPTMS) were purchased from Aldrich Chemical Co. (Milwaukee, WI).[1] *n*-Propyltrimethoxysilane (PTMS) and *n*-decyltriethoxysilane (DTES) were purchased from Gelest, Inc. (Tullytown, PA).[1] A.C.S. reagent grade acetone was used as the organic solvent, and distilled water as the reactant-cosolvent for the condensation reactions.

2.2. Methods

2.2.1. FTIR and NMR

Fourier transform infrared (FT-IR) spectra of the various organosilsesquioxanes and their polymeric products were obtained from 100 co-added scans at 4 cm^{-1} resolution with a Nicolet Magna 550 spectrometer[1] continuously purged with dry air. Spectra of the liquids, contained between Tl– (Br,I) plates, were recorded in the 4000 to 400 cm^{-1} region with a wavenumber expanded uncertainty of 1 cm^{-1}. ^1H nuclear magnetic resonance (NMR) spectra of the various organosilsesquioxanes and their polymeric products in $CDCl_3$ were obtained with a JEOL-GSX270 spectrometer.[1]

2.2.2. Mass spectrometry

Sinapinic acid was used as the MALDI matrix with acetone as the solvent for both the matrix and the analyte. Adventitious sodium and potassium were found to be the cationizing agents by close examination of the peak positions in the low mass region of the spectra where unit mass unit resolution was achieved [5]. Solution concentrations were typically 45 mg/ml for the matrix and 1.5 mg/ml for the analyte; however, acceptable spectra could be produced over a wide range of analyte to matrix ratios. These solutions were mixed in equal parts and electrosprayed [6] onto the target plate. Electrospraying was done at rates between 3 and 10 ml/min, from a fine steel capillary with a nominal

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[1] Certain commercial equipment is identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose.

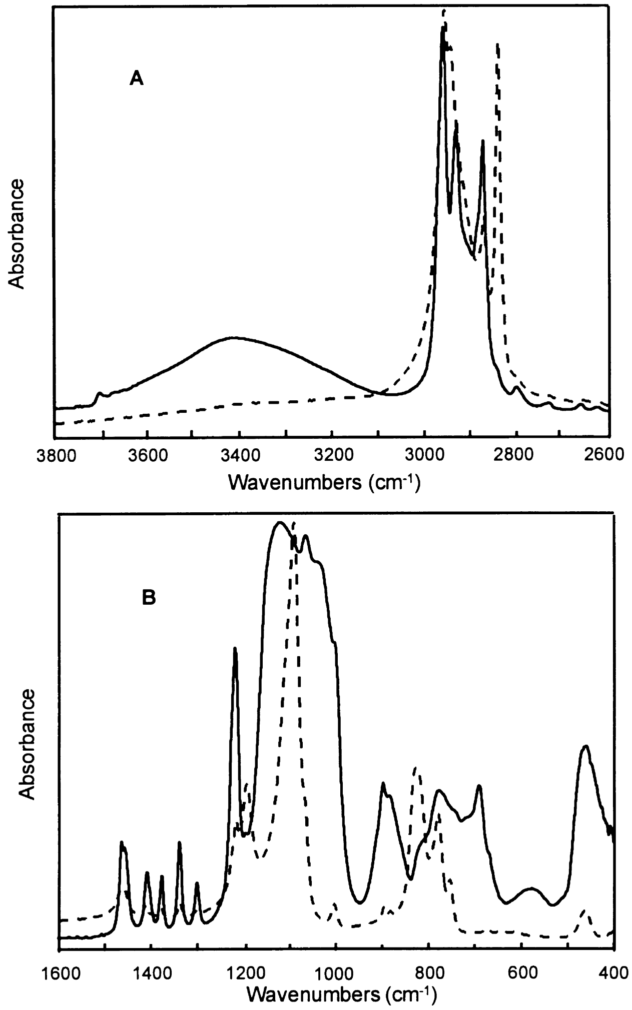

Fig. 2. Unnormalized Fourier-transform infrared spectrum of monomeric *n*-propyl silsesquioxane (PTMS) (dotted line) and of the polymeric *n*-propyl silsesquioxane (PPTMS) (solid line). Peak assignments are given in the text.

inner diameter of 0.56 mm held at 5 kV and located about 2 cm from the target plate. The thin electrosprayed films proved to be highly uniform giving good quality spectra at any site on the target.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry [7,8] was performed on a Bruker REFLEX II[1] in reflectron mode using delayed extraction. Ions were generated using a 337 nm wavelength nitrogen laser with a pulse duration on the order of 3 ns. As the electrosprayed mixture of matrix and analyte produced quite thin films, the laser was constantly rastered over the target to prevent exhaustion of a particular sample spot. Typically, only three to five individual laser firings would exhaust the target area. Thin electrosprayed films were shown to give higher resolution spectra than thicker films at the expense of having to raster the laser beam continually. All data shown are for positive ions: negative ion spectra typically produced only matrix ions and their clusters, e.g. M^-, $2M^-$, etc. The instrument was periodically calibrated with bovine insulin using the $[M + H]^+$ and $[M + 2H]^{+2}$ peaks. Much of the detail on sample preparation, instrument operation, and data analysis can be found in a previous publication [5].

2.3. Synthesis

2.3.1. Polymerization of MPTMS

In a glass vial was placed 1.00 g (4.03×10^{-3} mol) MPTMS; 0.277 g (15.4×10^{-3} mol) distilled water; 0.053 g (1.15×10^{-3} mol) formic acid and 2.60 g acetone. 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 0.732 g (mass fraction yield of 101%) of the polymerized MPTMS (PMPTMS) a clear, slightly pink, viscous liquid. PMPTMS was soluble in a number of common organic solvents (acetone, methylene chloride, tetrahydrofuran, and chloroform). FT-IR and ^{1}H NMR spectral analyses on the starting material and the polymer confirmed the loss of OCH_3 groups with the retention of the methacrylate ester group. FT-IR also indicated the formation of Si–O–Si structure and the presence of some residual Si–OH in the oligomer. The most notable features in the ^{1}H NMR spectra of the silsesquioxanes are related to the methoxysilane group. As the reaction proceeds, the sharp trimethoxy signal of the unreacted silane at 3.6 ppm is replaced by a broader methoxy signal at 3.5 ppm (expanded uncertainty, 0.02 ppm) due primarily to partially hydrolyzed and reacted silane. The methoxy signal gradually disappears and the remaining peaks in the spectra all show significant broadening that is indicative of a relatively high molecular mass product.

2.3.2. Polymerization of PTMS and DTES

The procedures to polymerize PTMS and DTES were similar to that described earlier. The polymerized product PDTES at 23°C is a slightly hazy liquid that on warming to 50°C forms a clear, colorless liquid, and solidifies on cooling at 5°C. By contrast, PPTMS is a clear, colorless highly viscous liquid. These oligomers were also soluble in common organic solvents. The polymeric structures were characterized by both FT-IR and ^{1}H NMR, which indicated virtually complete loss of the silyl ether groups.

2.3.3. Polymerization of PTMS without formic acid catalyst

In an open glass vial was placed 1.66 g (10.1×10^{-3} mol) of PTMS in a solvent system consisting of 1.00 g distilled water and 15.00 g of acetone. The solution was magnetically stirred at 23°C and the ensuing clear, colorless solution was allowed to concentrate. After 24 h, a second 16 g portion of acetone/H_2O was added and the evaporation process repeated. After 24 h, the residue was slightly more viscous and somewhat cloudy. The solvent addition–evaporation process was repeated and then after the 24 h period, the somewhat viscous liquid was heated at 65°C

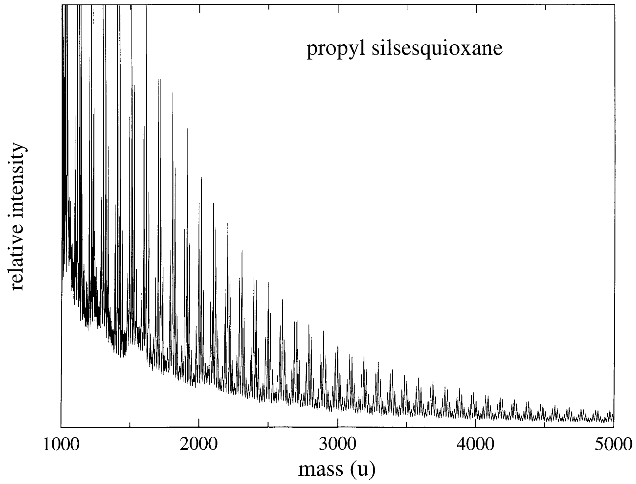

Fig. 3. The central portion of the full mass spectrum of the *n*-propyl silsesquioxane (PPTMS) material showing the characteristic shape of a condensation polymer. Estimated standard uncertainty of the peak position from calibration and repeatability studies is 0.2 u, and the estimated standard uncertainty in overall signal intensity from repeatability studies is 15%.

for an additional 17 h to yield a highly viscous liquid product. Characterization of this liquid by FT-IR and ^{1}H NMR indicated the complete loss of the OCH_3 groups. FT-IR also indicated the presence of residual silanol groups and the formation of Si–O–Si structure.

3. Results

The case of polymeric *n*-propyl silsesquioxane (PPTMS) will be described in detail, the analyses of the other polymers studied were very similar. Fig. 2 shows the unnormalized FT-IR spectrum of the PTMS monomer and of the PPTMS oligomer. In the top panel, the 2825 cm^{-1} band of PTMS, the CH_3 symmetric stretch of the OCH_3 groups, is overall absent in PPTMS along with reduced absorbance in the asymmetric CH_3 and CH_2 stretch region (~2950 cm^{-1}). The broad band from 3800 to 3000 cm^{-1} with maximum at ~3400 cm^{-1} in PPTMS is primarily ascribed to stretching of OH of Si–OH groups that are hydrogen bonded plausibly to other Si–OH groups and from water hydrogen bonded to itself and to the Si–OH groups. A small band near 3690 cm^{-1} is observed for “free” OH of Si–OH groups. In the bottom panel of Fig. 2, Si–O–CH_3 asymmetric and symmetric stretch bands of PTMS at 1088 and 817 cm^{-1}, respectively, are essentially absent in the spectrum of PPTMS, consistent with hydrolysis to form Si–OH groups and condensation of these to form Si–O–Si linkages. In the PPTMS spectrum, the shoulder around 900 cm^{-1} derives from Si– (OH) stretch, the bands at 1120 and 1043 cm^{-1} from Si–O–Si antisymmetric stretches, and an unassigned band at about 680 cm^{-1} is tentatively assigned to Si–O–Si symmetric stretch. Thus, the FTIR indicates all the O–CH_3 is gone in the PPTMS oligomer and only Si–OH remains. However, normalization to quantify how much silanol remains is difficult.

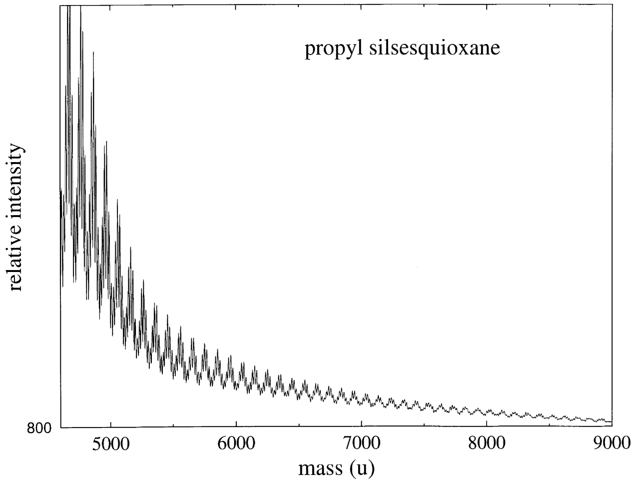

Fig. 4. High mass region for the *n*-propyl silsesquioxane (PPTMS) obtained by matrix blanking experiments. Oligomers could be detected up to about 9000 u for this material and to a similar value for the other polymers studied.

Fig. 3 shows the low-mass portion of the mass spectrum for *n*-propyl silsesquioxane (PPTMS), plotted as ion current at the detector versus ion mass. All spectra showed only singly-charged species as deduced from the peak positions and the isotope separations. For most samples studied the lowest oligomers detected were in the range of 1000 u, below this value matrix interference resulting from the MALDI process greatly complicates the mass spectrum. (Some matrix interference effects are seen in the baseline of Fig. 3 in 1000–1500 u range.) The overall shape of the mass spectrum is indicative of a condensation polymer. However, due to a variety of effects the molecular mass distribution (MMD) for such a broad molecular mass polymer is not considered reliable [9]. Fig. 4 shows the high mass oligomers for the same material, this time taken with matrix-blanking to prevent the low mass oligomers and the matrix ions from saturating the microchannel plate detector. Matrix-blanking is a method whereby fast moving (and, therefore, low mass) ions are prevented from reaching the detector by applying an electrostatic deflection bias along the ion flight path at short times after the laser pulse. Oligomers in this spectrum were observed up to 9000 u. Above this value the signal to noise ratio becomes such that the small peaks can no longer be identified. The overall structure of the MMD seems to be unchanged by the low mass blanking suggesting that detector saturation is not a major factor in determining the overall shape of the mass spectrum. However, it is not the overall MMD which is of interest in this paper. Rather, interest centers on the local mass distribution of each specific oligomer having *n* repeat units. It is expected that this local mass distribution is unchanged by the effects, such as detector saturation, which can cause the overall MMD to be in error.

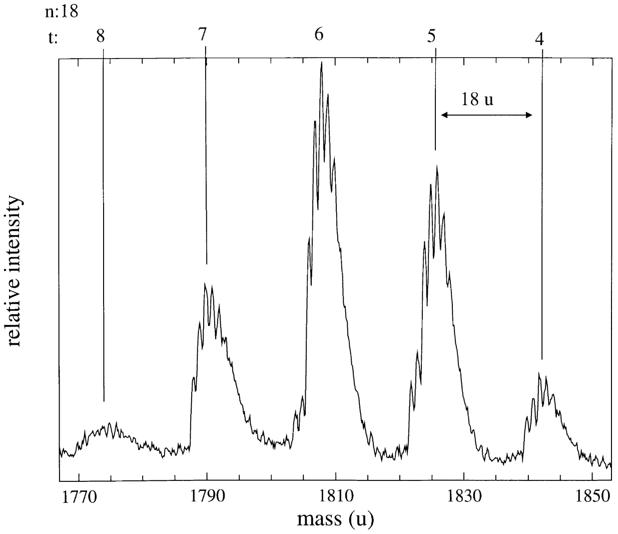

Fig. 5. Detail around a single oligomer of polymerized *n*-propyl silsesquioxane (PPTMS) from Fig. 3 for $n = 18$. Across the top of the figure is given the number of closed loops *t* indicated by the loss of water (18 u). The maximum value for *t* was 6 ($t_{max} = 6$) with the lowest *t* being 4 and the highest being 8.

Each major cluster of peaks in Figs. 3 and 4 corresponds to a single oligomer with a given number of repeat units *n*. As the monomer contains one silicon atom the value of *n* also corresponds to the number of silicon atoms in that oligomer. For PPTMS this average mass of the basic repeat unit is 104.1811 u. (The average is taken over all isotopes of each element present using their natural abundances.) This is the value of the mass difference between groups of peaks seen in Figs. 3 and 4. Knowing that ionization occurs via the attachment of Na^+, and by including the mass of the two $O_{1/2}H$ endgroups, an exact identification of each oligomer present in the sample can be made [5].

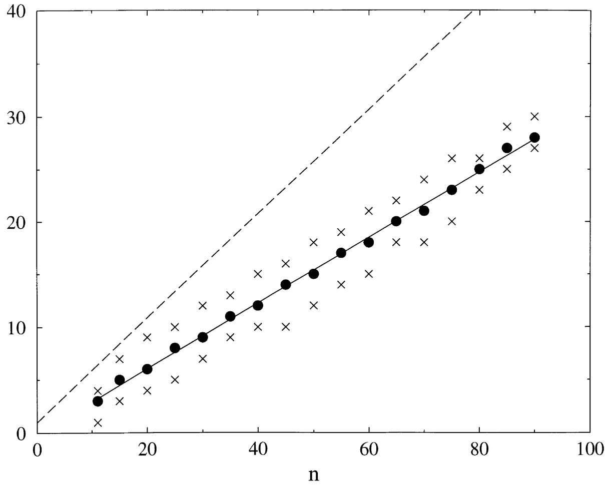

Fig. 6. A plot of t_{max} vs. *n* for the *n*-propyl silsesquioxane (PPTMS) data of Figs. 3 and 4. The solid circles are the values of t_{max} while the crosses are the lowest and highest value detected. The solid line is the linear regression fit to the values of t_{max}. The dotted line has a slope of 1/2 and represents the expected value for t_{max} in the case of complete condensation, that is, when no residual silanol groups remain. The actual slope of 0.311(4) indicates that this material has a molecular structure between fully-condensed polyhedra and highly-branched linear.

Fig. 5 shows the detail of a single low-mass oligomer from Fig. 3. The maximum possible mass of an oligomer with *n* repeat units occurs when every silicon atom has one silanol group in addition to one R-group and two bridging oxygen atoms. Two bridging oxygen atoms are the minimum number necessary for the formation of a polymer, that is, conceptually polymerization requires difunctionality at a minimum. Thus, the repeat unit in this case can be given as $[RSi(O_{1/2})_2OH]$. For an oligomer with *n* repeat units the mass of the heaviest oligomer is *n* times the mass of this "difunctional" oligomer (plus the mass of the Na^+ ion and the end groups). This heaviest oligomer is the linear or branched structure. However, the highest intensity peak generally does not occur at the maximum possible mass. Instead, lower mass peaks are more intense. These peaks correspond to the loss of water as a pair of Si–OH groups react. This in turn immediately indicates that *intramolecular* reactions are occurring. If *intermolecular* reactions were occurring the value of *n* would change and a new, higher mass, oligomer would be formed. In Fig. 5 $n = 18$ and the number of closed loops *t* is given across the top of the figure. The value of *t* ranges from 4 to 8 with 6 being the most likely value. Note that each peak is separated by 18 u indicating the loss of water.

Each loss of 18 u closes a loop in the molecule moving it away from a highly branched or linear structure toward a closed polyhedron. In the limit of the loss of all silanol groups a fully-condensed polyhedral structure results. For example, for $n = 8$ one possible fully-condensed structure is a cube with silicon atoms at each corner and Si–O–Si linkages for the cube edges. This involves the loss of four water molecules which we designate here as $t = 4$. For the example of $n = 18$ given in Fig. 5 the fully-condensed structure would result from the elimination of nine water molecules ($t = 9$). This specific oligomer was not observed in the mass spectrum. Thus, a plot of the maximum *t* for a given *n* can be used to determine the degree-of-intramolecular-condensation for a given silsesquioxane. Shown in Fig. 6 is such a plot for the *n*-propyl silsesquioxane mass spectrum shown in Fig. 3. The value of t_{max} vs. *n* as a function of *n* is linear indicating the relative number of closed loops, or degree-of-intramolecular-condensation, does not change as the molecular mass increases. This suggests that the local environment is the same with regard to degree-of-intramolecular-condensation at any place in the molecule and is independent of the size of the molecule. However, it should be noted that the type of mass spectrometry performed here does not give any information on the specific topology of a given oligomer, only whether or not it exists in detectable quantities. The dashed line in the figure has a slope of 1/2 which is the expected *t* vs. *n* ratio for fully-condensed oligomers and follows the equation $t = 1/2n + 1$ for *n* even, and $t = 1/2(n - 1) + 1$ for *n* odd. Conversely,

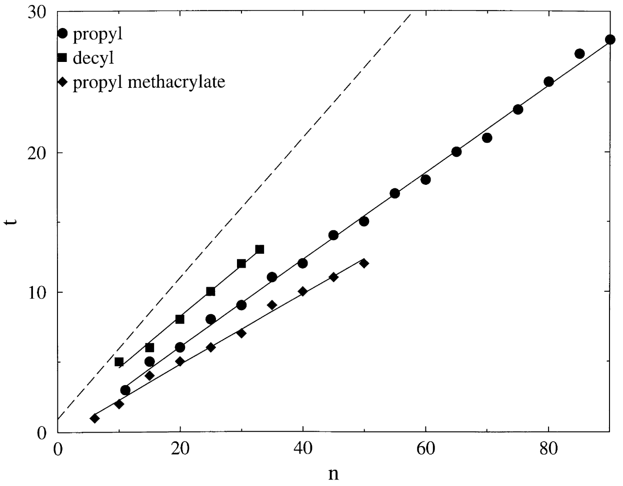

Fig. 7. A plot of t_{max} vs. n for n-propyl (circles), 3-methacryloxypropyl (diamonds), and n-decyl (squares) silsesquioxanes demonstrating that different R-groups yield different degrees-of-intramolecular-condensation for essentially the same synthesis conditions.

for a highly branched molecule showing no condensation $t = 0$ which corresponds the abscissa in Fig. 6. The n-propyl silsesquioxane considered in this example has a slope of 0.311, with a standard uncertainty of 0.004, a value that is between the fully-condensed and uncondensed polymer but leaning toward a more condensed structure.

This type of analysis was repeated for two other R-groups. The results for all three groups are plotted in Fig. 7. Clearly the degree-of-intramolecular-condensation is different even though the condensation reactions occurred under very similar conditions. Note, also, that the figure is plotted in terms of number of repeat units n not in terms of molecular mass thus giving the higher mass repeat units (e.g. the n-decyl silsesquioxane) a seemingly foreshortened mass range. In fact, each species had a maximum detectable molecular mass in the range of 8000–10 000 u. These observed differences in the degree-of-intramolecular-condensation among the different oligomers studied suggests that the R-group can play a role in determining where the gelation point occurs.

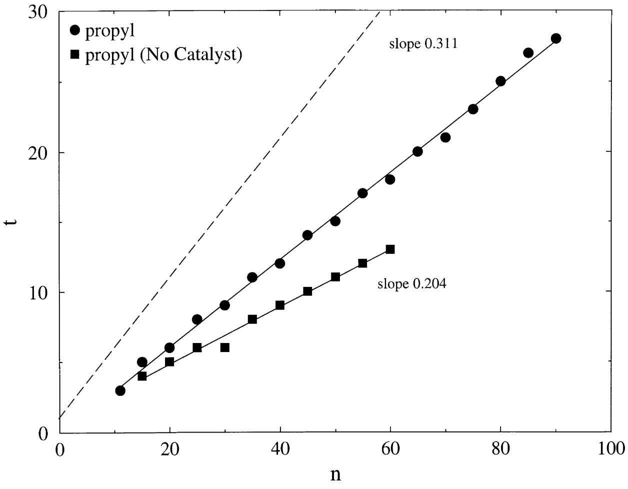

Fig. 8. A plot of t_{max} vs. n for n-propyl silsesquioxane prepared with and without the formic acid catalyst demonstrating the role of the catalyst in controlling degree-of-intramolecular-condensation as well as overall molecular mass.

Fig. 8 shows the degree-of-intramolecular-condensation for n-propyl silsesquioxane prepared with and without the formic acid as a catalyst. Two things become immediately apparent from this figure. First, the degree-of-intramolecular-condensation of the catalyzed reaction product is distinctly higher. Moreover, the total molecular mass achieved is also greater when the catalyst is used.

4. Discussion

Two issues come to light immediately as a result of these experiments: Why do different R-groups show different degrees-of-intramolecular-condensation even when prepared under the same synthesis conditions? Why do the specific R-groups studied give the observed degrees-of-intramolecular-condensation? To approach these question molecular aspects of the hydrolysis–condensation reaction are considered.

The synthesis reaction used involves two distinct steps that nevertheless occur simultaneously. The alykoxide ligands of the monomer first must be hydrolyzed. Next, the resulting silanol groups must condense to eliminate water. Anything that influences the rates of hydrolysis and/or condensation will have an effect of the final degree of intramolecular-condensation. For example, the details of solvation, coordination, and complexation of the monomer in the acetone/water mixture would have an effect on the hydrolysis rate. Differences in hydrolysis rate will influence the relative numbers of monomers having one, two or three silanol groups. In turn, these relative abundances will effect the condensation rate and the ultimate degree of condensation achieved.

Schmidt and Scholze [10] have reviewed how for tetra-alkoxysilanes the hydrolysis rate, as well as the gelation time, are strong functions of the length of the alkyl group of the alkoxy ligand: the longer this group the slower the hydrolysis and the longer the gelation time. This observation was attributed to changes in the partial charge on the silicon atom due to the different ligands. Complicating the analysis is the idea that this partial charge will change as the number of hydrolyzed groups increases and as the condensation reaction proceeds. This effect is difficult to quantify without real time spectroscopic information on the transient species present during the hydrolysis–condensation reaction.

In the case of the silsesquioxane experiments presented here many of the same arguments apply; however, now only three hydrolyzable alkoxy groups are present with the fourth ligand being the pendant R-group. As Schmidt and Scholze

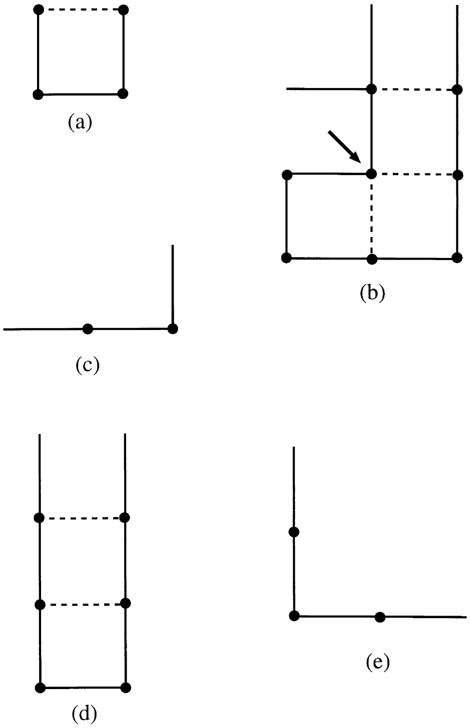

Fig. 9. Various possible short chains in a two-dimensional square lattice. Chain (a) shows the minimum number of bonds needed for chain closure, or for the first near-neighbor pair interaction. Chain (b) is the first example where the pair interaction model overcounts the possible closure for a functionality of three. The point with an arrow has functionality of four if all the dotted and solid lines were bonds. This problem has been considered in another context [18] and does not affect the linearity of the dependence of t on n. Chains (c) and (e) are examples of chains with no closure. Chain (d) is an example of a ladder.

[10] describe, estimating the partial charge difference on the silicon due to ligands of the Si–C type and the Si–O type is very difficult. Thus, while effects in the degree-of-intramolecular-condensation between different R-groups may be expected from partial charge arguments, how each group studied effects the partial charge on the silicon atom is hard to say.

A second difference between the R-groups studied concerns steric hindrance effects. It may be possible that the longer alkyl chains tend to exclude water from reaching the Si–O bonds and thus suppressing the hydrolysis reaction. Steric hindrance may also retard condensation by preventing silanol groups from coming into sufficiently close proximity to allow the elimination reaction to occur. However, examination of the data suggests that there is no simple trend in size of the R-group and the ultimate degree-of-intramolecular-condensation achieved. The smallest R-group, the propyl group, has a degree-of-intramolecular-condensation intermediate between the two larger groups, but in addition has oligomers with a substantially larger number of repeat units. This suggests a decoupling between the number of silanol groups left in a molecule and the ultimate size of the oligomers produced.

The fact that the 3-methacryloxypropyl silsesquioxane (PMPTMS) has the lowest degree-of-intramolecular-condensation suggest a third R-group effect: hydrogen bonding. In addition to silicon partial-charge effects and steric hindrance effects the carbonyl functionality in this R-group may hydrogen bond with the silanol groups and retard the condensation reaction. This would leave a product with a lower degree-of-intramolecular-condensation compared to the non-polar *n*-propyl and *n*-decyl groups. Evidence for this hydrogen bonding in PMPTMS was seen in IR data where various peak shifts were attributed to hydrogen bonding with silanol groups [11].

Another broad consideration brought to light by these results is: Why is the plot of $t_{\max}$ vs. n linear and not of some other functional form? When modeling multifunctional condensation reactions in carbon backbone systems [12,13] it has been common to assume only a few (e.g. two) ring closures per chain independent of chain length. Yet the data presented here suggest the number of ring closures is proportional to n and can become much larger than two ($t > 2$).

This linearity of $t_{\max}$ vs. n is consistent with most simulations and calculations on single polymer chains found in the literature. Consider the work of McCrackin, Mazur and Guttman [14], Mazur and McCrackin [15], and Douglas et al. [16,17] on the number of nearest neighbor interactions on an isolated polymer chain where the number of such individual interactions is used to estimate polymer–polymer intramolecular energetics. These nearest neighbor interactions for the simple case of a square lattice are shown as dotted lines in Fig. 9. In all of the studies cited the average number of nearest neighbor interactions is linear in n and is independent of synthesis conditions such as reaction temperature. This is because these interactions are understood to be the result of local structures and not long range effects. The connection is drawn to the current problem if the dotted lines in Fig. 9 are viewed as possible chain closures for growth by step reactions with molecules having the number of reactive functionalities equal to three. Thus from these and other Monte Carlo simulations of equilibrium or the non-equilibrium chains [18] it is expected that the local structure will affect the probability of ring closure and the number of rings should be linearly proportional to n.

The above discussion is true for a linear chain. Chains with long chain branching will have the same local structure and so the above arguments should hold. Chains with short chain branching should also have the same linearity since short chain branching increases the chain density and should allow for the same linearity in closures. In fact, one cannot get a power greater than one for the exponent on n. Increasing chain density (branching) should only increase the slope of our curve towards the maximum value of 1/2.

5. Conclusion

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-group was found to have a significant effect on the degree-of-intramolecular-condensation. Possible reasons for this include partial charge difference of the silicon atom, steric hindrance effects, or hydrogen bonding between silanol groups and the organic R-group. The absence of a catalyst in the polymerization of *n*-propyl silsesquioxane was found to not only influence the resultant molecular mass distribution but degree-of-intramolecular-condensation as well. Theories of step polymerization with monomer of functionality equal to three where shown to be consistent with the observation that the number of closed loops per oligomer, *t*, should be proportional to the size of the oligomer, *n*.

Broadly considered, these results point to a means to understand reactivity and gelation in silsesquioxanes and in condensation-reaction systems in general. While the traditional techniques of NMR and IR give semi-quantitative information on such issues as the average degree-of-intramolecular-condensation in the whole polymer, mass spectrometry gives more detailed information about specific oligomers. Ultimately it is envisioned that MALDI-TOF mass spectrometry will become an invaluable tool for the synthetic chemist in optimizing reaction conditions to produce desired final structures.

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