Substituent Effects on Microstructure and Polymerization of Polyalkylsilsesquioxanes

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Recently, there has been a great deal of interest in polysilsesquioxanes (PSSQs) for advanced technology as low-dielectric insulators in microelectronic devices[1,2] and novel reinforcing elements for nanocomposites.[3,4] PSSQs with the empirical formula $(RSiO_{3/2})_n$ are commonly synthesized from alkyltrialkoxysilane or alkyltrihalosilane through hydrolysis−condensation reaction, but the detailed molecular structures of PSSQ polymers are not well-known.[5] This is due to the fact that numerous covalently bonded polymer structures, such as cages, ladders, and random branches, can be formed by various combinations of intramolecular and intermolecular bond forming reactions starting from the trifunctional monomer. In this regard, understanding the structures of initial reaction products is very important, since they exhibit the tendency of various intramolecular versus intermolecular condensation reactions. This tendency determines the molecular structure and the molecular weight of the polymer products, which will eventually control the key physical properties. However, a detailed investigation of initial low molecular-weight PSSQ products has been hampered by the lack of a suitable analytical technique.

In this communication, we employ a novel graphite plate laser desorption/ionization time-of-flight mass spectrometry (GPLDI-TOF-MS) to directly observe silsesquioxane oligomers with various alkyl substituents, under 2000 Da, and show that the tendency to form closed cage-type structures increases with the size of alkyl substituents. Moreover, this result is then corroborated by measurements of time-dependence of relative molecular weights during the polymerization of various polyalkylsilsesquioxanes.

The polycondensation reaction leads to the formation of fully condensed polyhedral oligosilsesquioxanes (denoted as T_n), partially condensed cage structures ($T_n(OH)_m$), and open branched structures with multiple OH groups.[5−7] Extensive formation of cage structures without terminal hydroxyl groups, such as the cubic octamer and related prismatic structures, will limit further polymerization. Therefore, to control the microstructure and polymerization of PSSQs it is important to delineate the synthetic parameters that influence the formation of closed cage-type versus open branched oligomers. Previously, the synthesis of polyhedral silsesquioxane oligomers under selected reaction conditions was reported,[6−9] but there has been no systematic investigation on the influence of the organic substituents on the microstructure and polymerization of PSSQs.

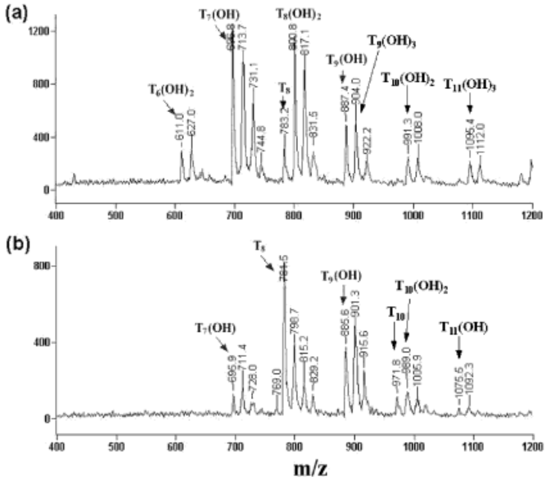

Figure 1. GPLDI-TOF mass spectra of propyl silsesquioxane oligomers produced after 5 (a) and 12 h (b), respectively, employing $r_1 = 1.0$, $r_2 = 5.0$ in refluxing 48% (w/w) THF solution at 65 °C (see the text).

Very recently, a direct observation of the initial condensation-reaction products comprised of low molecular-weight silsesquioxanes has been achieved with a GPLDI-TOF-MS method, which is a modification of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), employing a graphite plate instead of organic matrices to absorb the laser energy for desorption and ionization of the analyte.[10] Surprisingly, the initial study of PSSQs prepared from methyltriethoxysilane showed that the hydrolysis−condensation reaction results in open noncagelike structures.[10] Later experiments for the polymer prepared with methyltrimethoxysilane showed the same result, which is in contrast to the cagelike structures reported for PSSQs with different substituent groups.[6−9] It is therefore evident that the nature of the organic substituents plays an important role in determining the microstructure of PSSQs. Hence, a systematic study of PSSQs prepared with various alkyltrimethoxysilane monomers has been carried out.

The mass spectrum shown in Figure 1a, obtained with PE Biosystems (Framingham, MA) Voyager Biospectrometry workstation (337 nm nitrogen laser, 20 kV acceleration voltage, 1.2 m flight tube), shows sodium adduct ions of poly(propylsilsesquioxane)s prepared upon polymerization with an acid (HCl) catalyst for 5 h at 65 °C in refluxing THF solution under nitrogen atmosphere. Even though the signals were observed up to *m*/*z* 2000, strong peaks were clustered around 800. The small peak at *m*/*z* 783.2 corresponds to the fully condensed cubic octamer (T_8, expected at 784.1) similar to the hydrido-octamer[11] and *i*-butyl-octamer.[12] Partial-cage octamer $T_8(OH)_2$ was observed at 800.8. The peak at 817.1 is assigned to $T_8(OH)_4$. Condensed cages with an odd number of silicon atoms were also observed at 696.8 ($T_7(OH)$) and 887.4 ($T_9(OH)$). Figure 1b shows that upon polymerizing for an additional 7 h at 65 °C, intramolecular condensation converts the $T_8(OH)_2$ partial cage to the T_8 octamer. A pentagonal prism (T_{10}) is also shown at 971.8. The partial cage observed at 611.0 for $T_6(OH)_2$ in Figure 1a completely disappeared in Figure 1b without converting to the intramolecularly condensed, structurally strained trigonal prism (T_6); apparently, the $T_6(OH)_2$ partial cage underwent complete intermolecular condensation as the reaction progressed further.

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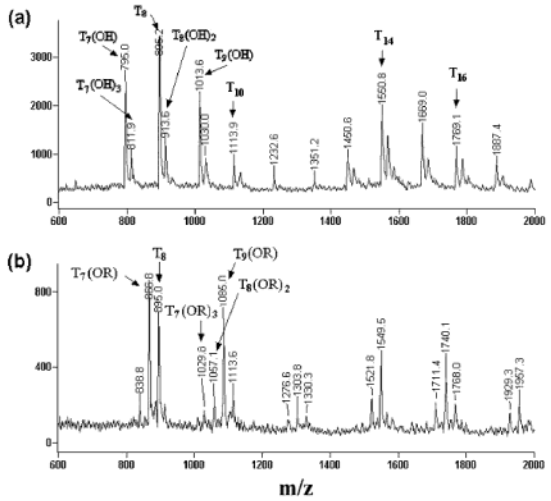

Figure 2. (a) GPLDI-TOF mass spectrum of isobutyl silsesquioxane oligomers produced after 8 days under the same condition as in Figure 1; (b) GPLDI-TOF mass spectrum of the sample in part (a) derivatized with trimethylchlorosilane.

Therefore, the structure of propyl PSSQs is significantly different from open branched structures of methyl PSSQs. It is likely that this difference arises from the steric and hydrophobic effects of the substituents. In other words, the bulkier and more hydrophobic propyl substituents tend to favor those conformations that place the propyl groups outside toward the organic solvent and the polar OH groups inward facing each other. Such conformations will then favor intramolecular condensation over intermolecular chain-extending reaction, leading to the preference of closed cagelike structures. This tendency will then become more pronounced for bulkier and more hydrophobic alkyl groups. In this regard, the simple pattern in Figure 2a from the isobutyl-substituted monomer, upon polymerizing for 8 days at 65 °C, indeed shows the predominance of fully condensed polyhedral oligomers, with the cubic octamer as the major species. Also, the apparent bimodal molecular weight distribution suggests that intermolecular condensation of partial cages with OH groups produces two cage-types connected to each other.

In addition, the presence of hydroxyl groups in the partial-cage oligomers from isobutyl monomer was analyzed by derivatizing them with trimethylchlorosilane for 1 h at room temperature. Figure 2b shows that derivatization of one hydroxyl group in the cage heptamer (T_7(OH), *m*/*z* 795.0) resulted in a 72 Da shift to *m*/*z* 866.8 ($-$OH to $-OSiMe_3$). The cage nonamer (*m*/*z* 1013.6) was also shifted to 1085.0. Derivatization of both hydroxyl groups in the partial cage octamer ($T_8(OH)_2$, *m*/*z* 913.6) produced a new peak at 1057.1. All three hydroxyl groups in $T_7(OH)_3$ (*m*/*z* 811.9) were derivatized to give a new peak at 1029.8. However, the fully condensed even-numbered cage-types (octamer (T_8) at *m*/*z* 895.2 and less abundant cage or connected-cage oligomers at *m*/*z* 1113.9 (T_{10}), 1550.8 (T_{14}), and 1769.1 (T_{16})) with no hydroxyl groups were not affected by the reaction with trimethylchlorosilane as expected. Therefore, these results confirm our structural assignments based on the observed *m*/*z* values.

Formation of highly condensed cagelike oligomers will have a major effect on the polymerization of PSSQs, analogous to the effect of cyclic oligomers in bifunctional polycondensation.[13] To explore this corroborative effect on polymerization, various alkyltrimethoxysilane monmers ($RSi(OMe)_3$, R = methyl, ethyl, propyl, and isobutyl) were polymerized in refluxing THF solution under nitrogen atmosphere. In this experiment, controlled molar ratios of HCl catalyst to alkyltrimethoxysilane (r_1) and water to alkyltrimethoxysilane (r_2) were employed to regulate the polymerization rate and the molecular weight as demonstrated previously.[14] The relative molecular weights (vs polystyrene standards) of growing polymers were then measured as a function of reaction time by gel permeation chromatography (GPC). When r_1 and r_2 were 0.03 and 10.0, respectively, methyl monomer produced polymers with weight-averaged molecular weight (M_w) of ~3000 after 6 h (see Figure 3a). However, monomers with alkyl substituents bigger than methyl did not yield high molecular weight products under the same reaction conditions. Instead their molecular weights leveled off around 600−700 within a relatively short time (ca. 2 h), as shown in Figure 3a.

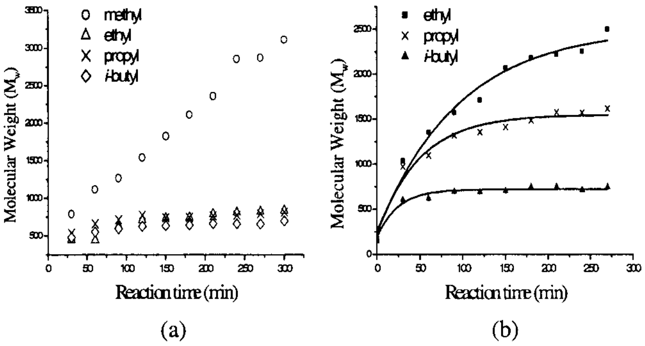

Figure 3. Variation of weight-averaged molecular weights of poly(alkylsilsesquioxane)s with reaction time in 48% (w/w) refluxing THF solution at 65 °C (a) with $r_1 = 0.03$ and $r_2 = 10.0$ and (b) with $r_1 = 1.0$ and $r_2 = 5.0$. The values are determined from GPC with polystyrene standard as a reference.

When a reaction condition strongly favoring the chain growth ($r_1 = 1.0$, $r_2 = 5.0$) was employed,[14] the polymerization of methyl monomer was too fast to control and insoluble gel products were obtained. In contrast, ethyl monomer yielded products with $M_w = 2500$ after 4.5 h and propyl monomer could be polymerized only up to $M_w = 1500$, while polymerization of isobutyl monomer did not progress beyond $M_w = 700$ (see Figure 3b).

Clearly, the overall polymerization of alkyltrimethoxysilane monomers is strongly influenced by the size of alkyl substituents. However, the initial increase in molecular weights during the first hour shows a relatively fast polymerization up to 6−10 monomers, nearly independent of the substituents. This indicates that the intrinsic reactivity of the Si sites does not vary significantly with the alkyl substituent. The large variation in further polymerization after the initial stage can then be considered to arise from the varying tendency of chain-extending intermolecular condensation, which depends on the microstructure and conformations of initial oligomers. Therefore, our results on polymerization strongly support the conclusion that the bulky alkyl substituents favor closed cage-type oligomers over open branched structures.

In summary, systematic GPLDI-TOF-MS experiments, along with GPC measurements of polymerization kinetics, show that the microstructure and polymerization of polyalkylsilsesquioxanes depend strongly on the alkyl substituents, with the tendency to favor closed cage-type structures increasing with the size of the alkyl groups. This is most likely due to the steric and hydrophobic effects of substituents on the conformations of initial oligomers, which control the rates of the intramolecular cyclization versus chain-extending intermolecular condensation reactions. This finding is expected to be very important in controlling the sol−gel chemistry of PSSQs[15] and synthesizing novel PSSQs for advanced technology.

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