



Separation and identification of oligomeric phenylethoxysiloxanols by liquid chromatography–electrospray ionization mass spectrometry



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ABSTRACT

Liquid chromatography–electrospray ionization mass spectrometry has been applied to qualitative analysis of oligomeric phenylethoxysiloxanols, a class of organosilanols as active intermediates to polyhedral silsesquioxanes. The phenylethoxysiloxanol samples were prepared by controlled acid-catalyzed hydrolysis and condensation of phenyltriethoxysilane at various molar equivalents of water (r_1) and characterized by standard spectroscopic techniques. Using a gradient binary water–methanol mobile phase, these reaction products were resolved on octadecylsiloxane silica stationary phase and subsequently identified by online electrospray ionization mass spectrometric detection. Results show that the reaction products are composed of a multitude of linear and monocyclic siloxanol oligomers with various numbers of silicon atoms and hydroxyl groups, depending upon the reaction conditions used. With the r_1 value increasing from 0.5 to 2.0, the chain lengths of the oligomers increase slightly but the numbers of hydroxyl groups increase considerably, accompanying by structural evolution from chains to rings. Characterization of the retention behavior of these oligomers indicates that hydrophobic interactions of phenyl and ethoxy groups with the stationary phase are responsible for their retention in reversed-phase liquid chromatography.

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1. Introduction

With the quest for innovative advanced materials, enormous efforts have been directed to development of organic–inorganic hybrid materials that promise to combine hardness and stability of inorganic glasses with flexibility and low-temperature processing of organic polymers [1,2]. An interesting class of these materials is derived from silsesquioxane, an organosilicon compound with the empirical chemical formula $\text{RSiO}_{3/2}$ where R refers to alkyl/aryl or organofunctional groups. A wide variety of silsesquioxanes in ladder, cage and cube forms have been synthesized and used as building blocks for nanocomposites in optoelectronics, heterogeneous catalysts, nanoglobular drug carriers, and other promising applications [3–5]. Typically, silsesquioxane based hybrid materials are prepared by acid- or base-catalyzed hydrolysis and condensation of the organo-modified trifunctionalsilane, also known as sol-gel process. This process proceeds from partial hydrolysis of the organosilane to form reactive silanol monomers, to condensation of these monomers to result in oligomers (sol formation), and finally to polymerization by crosslinking of the oligomeric

species leading to a three-dimensional network (gel formation) [6,7]. Detailed knowledge about the oligomeric species present in solution is mandatory to understand the chemistry of the process and to tailor the properties of the product.

The solid product can be characterized by a variety of techniques including electron microscopy, physisorption, porosimetry, infrared (IR), and ^{29}Si nuclear magnetic resonance (^{29}Si NMR) spectroscopy. However, studies of soluble oligomeric silanols in solution have proved to be challenging because only a few techniques are suited for such analyses such as gas chromatography (GC), ^{29}Si NMR spectroscopy, and electrospray ionization mass spectrometry (ESI-MS) [8–10]. For GC analysis, the silylation of the oligomeric silanols with alkytrichlorosilanes is required to facilitate their transfer to the gas phase. This process usually requires the use of acid- or base-catalyst and produces side reactions such as polymerization or depolymerization of the silicate species. Since the method requires a relatively long time range, and the modification of the reaction mixture, it is more useful for studying trends but not appropriate for the investigation of the oligomer distribution. Identification of the silicate species by ^{29}Si NMR is based on the characteristic chemical shifts of ^{29}Si atoms resulting from the distinctive shielding effects of the chemical bonds attached to the silicon atoms. Despite the long tradition of using this technique for characterization purposes, some disadvantages are inherent to

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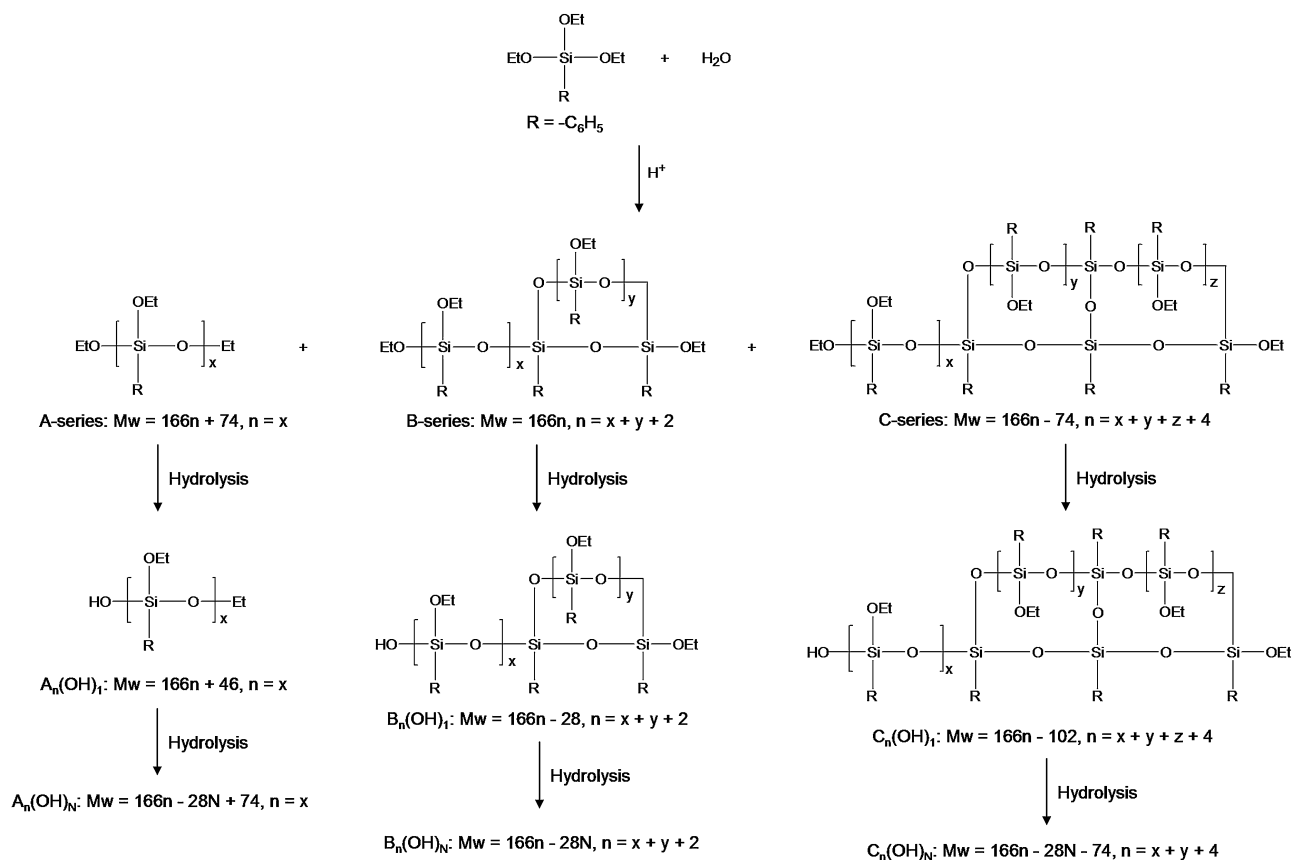


Fig. 1. Controlled acid-catalyzed hydrolysis and condensation of phenyltriethoxysilane to produce phenylethoxysiloxane and phenylethoxysiloxanol oligomers where n represents, respectively, the number of repeat units in the linear species (A-series) and the sum of the silicon atoms x , y and z in the cyclic species (B- and C-series).

the ^{29}Si NMR experiments. First, ^{29}Si NMR experiments are time consuming owing to both the low natural abundance of ^{29}Si nuclei and its small and negative magnetogyric ratio. This technique is inappropriate for quantitative measurements in systems with fast evolution because of the use of long recycle delays. Second, spectral interpretation is difficult for complex systems owing to peak overlapping of the ^{29}Si signals. In contrast, ESI-MS is a fast, sensitive, and selective analytical technique that allows for rapid screening of silicate oligomers in solution. Detection and quantification of analytes are based on measurements of the mass-to-charge ratio (m/z) and intensity of the target ions produced in the ESI source. A distinct advantage of ESI is that little fragmentation occurs to thermally labile species, thus simplifying the assignment of the signals and interpretation of the spectra. This technique has been applied to identify the silicate species and to monitor the temporal evolution of oligomers in acid and basic media [9]. Like all other techniques, however, ESI-MS is not without limitations. First, single stage MS is unable to distinguish geometric isomers of silicate oligomers, which increases with the number of silicon atoms in the molecule [11]. Second, ion suppression resulting from the presence of species in the sample which compete for ionization or inhibit ionization in other ways introduces great uncertainty in quantification of analytes, leading to biased oligomer distribution [12]. Obviously, there is a demand for a viable alternative method to overcome limitations inherent in the analytical techniques currently available.

High-performance liquid chromatography (HPLC) has been widely used in oligomer analysis with a potential capability to resolve isomers [13–15]. Initial studies by Dorn and Skelly Frame demonstrated the speciation and quantification of organosilicon compounds by HPLC with inductively coupled plasma-atomic

emission spectrophotometry (ICP-AES) [16]. As degradation products of poly(dimethylsiloxane) polymer, water soluble silanol oligomers ranging from monomer to trimer were baseline separated by reversed-phase HPLC with water-acetonitrile as mobile phase and detected by ICP-AES with high sensitivity. This approach was extended by using ICP-MS as a detector allowing for detection of silanol species at lower levels [17]. Most of the work reported to date, however, has been limited to the determination of very low molecular weight silanols in environmental and industrial samples. Moreover, HPLC-ICP is not suited for studies of oligomer distribution because it requires the use of reference standards for identification, which are unfortunately not available in most cases. Recently, we showed for the first time that HPLC coupled with ESI-MS (LC-ESI-MS) can be used to separate and identify oligomeric siloxanes derived from acid-catalyzed hydrolytic condensation of vinyltrimethoxysilane and to monitor the structural evolution of the oligomers with the amount of water in the reaction mixture [18]. Results from this work revealed several advantages of this approach over the conventional ones. First, separation and identification of oligomers can be done simultaneously allowing for broad range of complex samples to be addressed. Second, resolution of isomeric compounds is achievable by the chromatographic separation, facilitating their identification by subsequent MS detection. Furthermore, ion suppression effects in LC-ESI-MS are reduced by the sample dilution occurred during the chromatographic process.

Herein, we extended this approach to characterize oligomeric silanols as active intermediates to polyhedral silsesquioxanes and to study their retention behavior in gradient reversed-phase chromatography. We chose phenyltriethoxysilane (PhTES) derived silanols as model compounds because they are active intermediates

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