Separation and identification of oligomeric vinylmethoxysiloxanes by gradient elution chromatography coupled with electrospray ionization mass spectrometry

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ABSTRACT

A high-performance liquid chromatography with online electrospray ionization mass spectrometry (HPLC–ESI-MS) has been used to separate and identify the reaction products resulting from controlled acid-catalyzed hydrolytic polycondensation of vinyltrimethoxysilane (VMS). The reaction products were prepared in the molar ratio of water to VMS (r_1) ranging from 0.6 to 1.2, characterized by standard spectroscopic techniques, and subsequently analyzed by HPLC–UV absorbance detection and HPLC–ESI-MS. Linear vinylmethoxysiloxane oligomers with the number of repeat units (n) ranging from 3 to 11 are predominant species at the beginning of the reaction (for $r_1 = 0.6$). Then they transform into monocyclic (for $r_1 = 1.0$) and bicyclic (for $r_1 = 1.2$) species with gradually increasing amount of water in the reaction mixture. The oligomer conversions suggest that structure growth of vinylmetoxysiloxanes proceeds by nonrandom cyclization reactions, which are favored over chain extension under the chosen reaction conditions. Direct ESI-MS, HPLC–ESI-MS and HPLC–UV were used to determine the molar mass distributions for the vinylmethoxysiloxane oligomers prepared in three different values of r_1. The molar mass averages increase slightly with the amount of water in the reaction mixture and vary somewhat with the method used. Our results indicate that with the combined capability of separation, sensitivity and identification, HPLC–ESI-MS is especially useful to study highly complex silicon-based compounds with hyperbranched, caged or cubic structures as building blocks for hybrid materials.

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1. Introduction

Hybrid materials with organic–inorganic character are advanced functional materials which represent not only a new field of basic research but offer prospects for many applications in diverse fields [1,2]. Organic–inorganic hybrid materials can be defined as nanocomposites with covalently bonded organic and inorganic components. Typically, they are obtained through hydrolysis of organically modified silicon alkoxides condensed with or without simple metallic alkoxides. Polycondensation results in a variety of structures ranging from monodisperse silica particles to polymer networks depending on the reaction conditions used. In addition, copolymerization of alkoxysilanes of variable functionality makes it possible to tailor the structure, morphology, and properties. Tetrafunctional alkoxysilanes form densely crosslinked silica structures, trifunctional monomers polymerize to branched or cagelike silsesquioxanes and

bifunctional alkoxysilanes yield linear polysiloxane chains increasing the elasticity of a material [3].

Hybrid materials can be classified based on the possible interactions connecting the inorganic and organic species [1]. Class I hybrid materials are those that show weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components. Class II hybrids are formed when the discrete inorganic building blocks are covalently bonded to the organic polymers. Today the main hybrid materials that find industrial applications are based mostly on class II hybrids for their improved homogeneity and durability. Organofunctional trialkoxysilane monomers of higher compatibility with organic polymers are commonly used to prepare hybrid polymers, especially as coupling agents in coating materials [3,4] and glass fillers in dental restoratives [5].

Vinyltrimethoxysilane (VMS) is an organofunctional alkoxysilane monomer that can undergo both the sol–gel polymerization of the alkoxy groups and curing of the vinyl functionality to

form a hybrid network with covalent bonds between organic and inorganic phases. This property of VMS has been exploited for preparation of flexible thin films with variable tensile strengths [6–8] and hybrid monolithic capillary columns for applications in separation science [9–11]. Condensation products of acid-catalyzed hydrolysis of VMS with various molar equivalents of water in the reaction mixture have been characterized by size exclusion chromatography (SEC), infrared (IR), ^{29}Si nuclear magnetic resonance spectroscopy (^{29}Si NMR) [6–8]. A recent report by Zhang et al. describes the use of matrix-assisted laser desorption/ionization mass spectrometry (MALD–MS) to identify complex oligomeric species present in the hydrolytic reaction [12]. They confirmed the presence of polyhedral cagelike structures and incompletely hydrolyzed/condensed ladder structures, containing 5–20 silicon atoms. However, since single stage mass spectrometry does not provide any information about the specific arrangement of atoms, it is impossible to distinguish structural or geometric isomers which are known to be abundant based on experimental and theoretical investigations [4,13]. Tandem mass spectrometry experiments or chromatographic separation methods prior to soft ionization mass spectrometry analysis is generally required to resolve isomers for better control of the hydrolytic condensation reaction and understanding of the chemical pathways for cage or ladder formation. Up to date there is no published report on the use of liquid chromatography other than SEC for separation of the oligometic reaction products from hydrolytic condensation of trialkoxysilanes.

Molar mass averages and molar mass distributions (MMDs) are important parameters for characterizing oligomeric/polymeric precursors as they provide the basics for chemical and physical properties as well as the mechanism of polymerization. These parameters are conventionally determined by SEC based on polystyrene standards for molar mass calibration. The last decade, however, has witnessed an increased use of the MS-based methods for oligomer/polymer characterization, primarily because MS provides much greater resolution than SEC and does not rely upon polystyrene standards [14–16]. Nevertheless, their potential in characterizing silsesquioxane precursors has yet to be demonstrated.

In this work, we describe a high-performance liquid chromatography coupled with electrospray ionization mass spectrometry (HPLC–ESI-MS) method for the separation and identification of vinylmethoxysiloxane oligomers as intermediates to polyhedral silsesquioxanes. We start with the preparation of the oligomers of different morphologies by controlled acid-catalyzed hydrolytic condensation of vinyltrimethoxysilane and their characterization by standard spectroscopic techniques. Then we proceed with the HPLC method development for the separation of oligomers and their online MS identification. Finally, we compare the molar mass averages and distributions determined by direct probe ESI-MS, HPLC–ESI-MS and HPLC–UV absorbance to demonstrate the relative performance of these methods.

2. Experimental

2.1. Chemicals

Methanol (HPLC grade) and hydrochloric acid (Analytical grade, 37 wt% HCl) were purchased from Concord Chemical Reagents (Tianjin, China). Vinyltrimethoxysilane (VMS) was obtained from WD Silicone (Wuhan, Hubei, China).

2.2. Preparation of oligomeric vinylmethoxysiloxanes

The vinylmethoxysiloxanes were synthesized by following the literature procedure with minor modification [7]. Briefly, a mixture of VMS (12.7 g, 0.085 mol) and methanol (7 mL) was added to a three-necked round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and an outlet. This mixture was cooled in an ice bath for 10 min. The water and hydrochloric acid were mixed in the molar ratio of H_2O to VMS, r_1, in the range of 0.60–1.2 and the molar ratio of HCl to VMS, r_2, fixed at 0.035 and added dropwise over a period of 5 min to the methanol solution of VMS under vigorously stirring. Upon completion, the final mixture was brought to room temperature and stirring was continued for 10 min. A regulated nitrogen gas flow was supplied and the mixture was heated at 70 °C for 3 h with continued stirring at the rate of 150 rpm. Viscous liquids weighed 7.5, 7.1, and 6.5 g were obtained for $r_1 = 0.6$, 1.0 and 1.2, respectively.

2.3. Structural characterization

The infrared (IR) spectra of vinylmethoxysiloxanes were acquired on a Tensor 27 FTIR spectrophotometer (Bruker Optics, Ettlingen, Germany) using KBr pellets. ^{29}Si NMR spectra were acquired on a Varian InfinityPlus-300 MHz spectrometer equipped with a 7.5 mm double-resonance MAS probe operating at 59.56 MHz with a 90° pulse width (Palo Alto, CA, USA). The neat liquids of vinylmethoxysiloxanes were transferred into PE tubes for spectral measurements. Direct ESI mass spectra were acquired on an Agilent 6310 ion trap mass spectrometer equipped with an electrospray ionization interface (Waldbronn, Germany) operated in the positive ionization mode. The ionization parameters were set as follows: dry temperature, 350 °C; nebulizer gas, 30 psi; dry gas flow, 8 L/min; HV capillary voltage, 3.85 kV. The capillary exit block and skimmer voltages were set at 142 and 40 V, respectively. The ESI-MS instrument was controlled by Agilent ChemStation and the signals were acquired and processed by Bruker Compass DataAnalysis 4.0. The mass spectra were recorded in the m/z range of 200–2200. A 10-µL aliquot of the methanol solutions of vinylmethoxysiloxanes at 100 mg/ml was introduced directly into the ionization source at 0.4 mL/min with flow splitting ratio at 1:2.

2.4. Chromatographic separation

An Agilent 1200 Series HPLC system consisting of a degasser, a quaternary pump, column oven, autosampler, UV–visible wavelength absorbance detector, and ESI-ion trap mass spectrometer was used throughout. Separations of the vinylmethoxysiloxane oligomers were carried out on a BaseLine C_{18} column (250 mm × 4.6 mm I.D., 5 µm particle size, 100 Å pore size) at 30 °C (BaseLine Chromtech Research Center, Tianjin, China). A binary solvent system consisting of water (solvent A) and methanol (solvent B) was used in linear gradient mode from 80% to 100% B over 40 min and then held at 100% B for 10 min. The flow rate was 1 mL/min. The UV wavelength was set at 215 nm. An injection volume of 10-µL was used for HPLC analysis. The online ESI-MS conditions were the same as for direct ESI-MS experiments.

2.5. Data analysis

The number- and weight-average molar masses, M_n, M_w, of vinylmethoxysiloxanes synthesized under various conditions and their corresponding degrees of polymerization, n_n, n_w, are calculated by the following formulas:

$$M_n = \frac{\sum c_i}{\sum (c_i/M_i)} \tag{1}$$

$$M_w = \frac{\sum (c_i M_i)}{\sum c_i} \tag{2}$$