Journal of Molecular Structure 1175 (2019) 367–372

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Structural studies of polycrystalline octavinyloctasilsesquioxane – $(C_2H_3)_8Si_8O_{12}$

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A R T I C L E I N F O

Article history:
Received 22 May 2018
Received in revised form
27 June 2018
Accepted 28 July 2018

Keywords:
Octavinyloctasilsesquioxane
Crystal structure
Molecular structure
X-ray powder diffraction
Infrared spectroscopy

A B S T R A C T

The structure of polycrystalline materials may differ significantly from that determined from monocrystalline studies. The combination of measurement and calculation techniques is one of the most effective ways to determine structural differences. The use of x-ray powder diffraction (XRD) supported by Monte Carlo calculations as well as complementing these studies with Fourier-transform infrared spectroscopy (FTIR) supported by *ab initio* calculations helped to determine the structure of octavinyloctasilsequioxane as a powder specimen. The results show a rhombohedral distortion of the cubic-shaped molecule along the ternary axis of the unit cell. Monte Carlo calculations support the model wherein vinyl groups at the Si atom sites along the C_3 axis could be located at one of the three equivalent positions, with the possibility of rapid reorientation. XRD measurements, as a function of temperature, show structural transition from a hexagonal (rhombohedral) to a low symmetry (probably triclinic) orientation, but through an intermediate monoclinic space group.

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1. Introduction

Silsesquioxanes are organosilicon compounds belonging to the siloxane group. They are made up of so-called T units – that is, structures wherein a silicon atom is bound with one and a half oxygen atoms (three oxygen atoms at silicon). The general formula for silsesquioxanes is R $(SiO_{1.5})$, where R is an organic substituent. The structure of silsesquioxanes depends on reaction conditions, and they can assume three-dimensional cage-type shapes or two-dimensional ladder-like structures. This classification was created on the basis of the dimension of the inorganic core (i.e., the structure containing *n* number of T units). Commonly, these compounds are therefore marked with the symbol T_n. The most common compounds of this class are T_6 (hexasilsesquioxanes), T_8 (octasilsesquioxanes) T_{10} (decasilsesquioxanes), and T_{12} (dodecasilsesquioxanes).

For more than a half a century, silsesquioxanes have drawn increasing attention for their unique combination of organic–inorganic properties and, therefore, their manifold application possibilities [1–5]. For this reason, it is extremely important to distinguish the structure underlying all their chemical and physical properties. An unambiguous and direct determination of the structure is possible with the use of single crystal diffraction. Unfortunately, it is not always possible to process a single crystal of sufficient size and, simultaneously, a small number of defects. In addition, the structure of a single crystal does not necessarily reflect the structure of the polycrystalline compound, which is the one used most often in its applications. Moreover, for this, the use of x-ray powder diffraction in combination with computational methods is an increasingly popular method for determining the structure of organic molecular [6–8] as well as inorganic ionic [9] crystals.

This paper presents results of the structural research on polycrystalline octavinyloctasilsequioxane (T_8^{Vi}). Similar to previous research on hydrogen-terminated silsesquioxane [10], we aimed to prove the efficiency of combined powder diffraction studies and infrared spectroscopy in resolving structural details. The results based on the measured FTIR spectra were used to correct molecular model applied for XRD fitting and vice versa. This is especially applicable if both long- and short-range sensitive methods are supported by *ab initio* calculations. In the previous structural studies on single crystalline form of vinyl terminated octasilsesquioxane [17,18], there are uncertainties to the exact position of the vinyl moieties at the ternary molecular axis and at the general position as well. This is due to the major drawback of the proposed model based on the assumption that the silicon-oxygen

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https://doi.org/10.1016/j.molstruc.2018.07.104

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cage has a cubic symmetry. In this work, we have successfully attempted to solve the ambiguity in the determining the positions of vinyl groups. A new proposed model of the molecule is the result of the agreement between calculations and experimental data fitting. Moreover, almost no constraints on the molecular shape were applied in order to achieve most coherent results with the space group symmetry.

2. Experimental

Entire studies were conducted on commercially available $(C_2H_3)_8(SiO_{1.5})_8$ – octavinyloctasilsequioxane (T_8^{Vi}) – available in the form of a white powder. The compound is available through two major suppliers (Merck [formerly Sigma-Aldrich] or Hybrid Plastics), but we found no differences in measurements for compounds bought from each company. However, for clarity of the studies, we have chosen the Merck product, and all reported results relate to the product from this manufacturer.

Powder diffraction measurements were conduct by using a PANalytical X'Pert Pro MD diffractometer that employed a Cu $K_{\alpha 1}$ x-ray line with the Bragg–Brentano standard setup comprising a Ge (111) Johansson monochromator at the incidence beam. The scanning range was 8°–70° with 0.008° step size and 20 s measurement time for each step. During the measurements, the samples were spun along an axis parallel to the scattering vector to neglect the effects associated with the development of a preferred orientation. All measurements in structural studies were conducted at room temperature. In case of low-temperature measurements, for technical reasons, the diffraction setup excluded the Johansson monochromator which was replaced by a Ni filter in front of the detector.

Subsequent cycles of the reverse Monte Carlo direct space method and full-pattern fit (Rietveld refinement) were used to resolve the T_8^{Vi} structure. *FOX* (version 1.9.7) [11] provided the code for Monte Carlo calculations, and PANalytical *HighScore Plus* (version 3.0e) was use to conduct the Rietveld refinements.

The spectra of T_8^{Vi} in the middle and far-infrared range were measured using the KBr pellet technique with a resolution of 4 cm^{-1} using a Bruker 70 V infrared spectrometer that was equipped additionally with the silicon beamsplitter for measurements in the far-infrared region. The sample in powder form, similarly as for the diffraction measurements, was applied to a KBr window (or polyethylene for the far infrared) to obtain a smaller Christiansen effect than the standard KBr pellet technique. Positions of the measured spectrum bands were determined by using a smoothed second derivative (Savicky–Golay filter using 19 points).

Calculations of infrared spectrum for the isolated molecule (molecular model) were derived using Gaussian 09 software. The T_8^{Vi} molecule was subjected to an energy-minimization procedure. The B98 (Density Functional Theory) method and a set 6-31G(d) of basis functions were used. Calculations of infrared spectrum of the periodic model (assuming crystal symmetry) were obtained using CRYSTAL 14 software [12] after the energy-minimization procedure by the B3LYP (DFT) method and the following set of basis functions: Si (88-31G(d)) [13], O (6-31G(d)) [14], C (6-32G(d)) [15], and H (3-21G) [16], which are optimized for applied code and periodic structures. Furthermore, the result of the calculations provided the infrared intensities of the normal modes. The equilibrium positions of the atoms and their displacements vectors for each normal-mode sinusoidal trajectory of the atoms was calculated. On the basis of the calculated frequencies and intensities, an infrared spectrum was constructed by assuming a 30 cm^{-1} band half-width. Calculated frequencies were scaled using a scale factor of 0.96. A similar calculation procedure was uses, with successful results as in previous research [10].

3. Results and discussion

In Fig. 1, the red dotted line shows diffraction patterns measured at room temperature. The figure inset represents a narrower range to emphasize low-intensity reflections. The black solid line presents the final full-pattern fit constructed according to the proposed structural model, as discussed further.

The structure derived from a single crystalline material could differ from the structure of the powder specimen. Apart from the obvious reasons resulting from the measurement technique and the loss of information on the scattering vector direction, the differences may be present in the material structure itself. In the powder specimen, where crystallites are of a micron order of magnitude in diameter, the internal heterogeneous stress may alter interatomic distances in a certain direction, as observed previously [10]. Therefore, a full-pattern fit of the powder diffraction data based on the single crystalline structure does not give satisfactory results. This is so in the case of the matching structure of T_8^{Vi} taken from the results of research conducted by Bonhomme et al. [17]. The low correlation between the model and the measurement ($R_{wp} = 32.631$; GoF = 89.632), which arises from the poor relative intensity match rather than the diffraction line positions, indicates that the symmetry of the T_8^{Vi} molecule is distorted. The space group symmetry $R\overline{3}$ ($^2C_{3i}$) as well as the unit cell dimensions published by Bonhomme et al. were used as a starting point for the Monte Carlo simulation. To preserve the site symmetry of the molecule in the trigonal unit cell, the quasi-molecule was created by taking a fragment of the T_8 unit, which consisted of two silicon and two oxygen atoms. In addition, to fulfill the unit cell symmetry and the requirements thereof, two separate vinyl molecules were included in the model, with both missing one of the hydrogen atoms. Because one of the vinyl group should position itself along the C_3 axis, the one-third occupancy was predetermined for one of vinyl moiety. No constraints have been imposed between those three entities although each was rigidified in the beginning of the simulation process. The parallel tempering algorithm was applied to match the simulated positions of atoms with the measured diffraction pattern. As the results of the simulation reached the local minimum, constraints were systematically removed from the rigidified units. The only constraints left were C–H distances (1.00 ± 0.1 Å) and angles, because the hydrogen atom has a negligible small scattering cross-sectionally for x-rays and does not contribute to the diffraction pattern. Finally, the last run of the Monte Carlo simulation was followed by the final Rietveld refinement, where thermal displacement parameters of all atoms

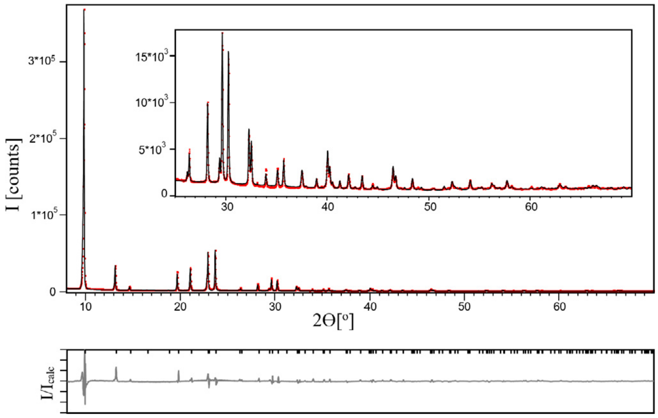

Fig. 1. Powder diffraction pattern (red dots) of ocavinyloctasilsesquioxane under ambient conditions along with fitted model (black line). The inset illustrates enlarge section to emphasize low intensity details.

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