

DFT study of vibrational dynamics and structure of aminopropylsiloxane polymer

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Received 6 October 2006; received in revised form 3 November 2006; accepted 6 November 2006

Available online 11 December 2006

Abstract

In this work, we investigated IR and Raman spectra from 400–1800 cm⁻¹ of aminopropylsiloxane (APS) polymerized on PVC substrate at room temperature. Complete assignment of the vibrational spectra was carried out using density functional theory calculations with Becke's three-parameter exchange functional in combination with the Lee–Young–Parr correlation functional (B3-LYP) and standard 6-311++ G(d,p) basis set. The vibrational spectra were calculated for two different conformations of silicoxygen rings: ladder structure and cubic structure. Comparative analysis of calculated and measured spectra reveals that ladder structure has been formed at the surface of PVC support.

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Keywords: Aminopropylsiloxane; DFT; Ladder; Vibrations

1. Introduction

Aminopropylsiloxane is an organosilane coupling agent whose capacity of adsorption on different materials is frequently used for functionalization of surfaces like optical fibers [1], nanoparticles [2,3], semiconductors or metals [4]. These molecules can form various kinds of bonds with the surface of substrate, changing thus their mechanical, optical or electrical properties. The nature of these bonds depends greatly on the conformation of the polymerized structure. Controlled hydrolysis followed by polycondensation of silanes provides polysiloxanes with various shapes including cyclic, linear, ladder like and cubic structures.

Handke and his coworkers analyzed vibrational spectra of silicates and siloxanes proposing a model of silicoxygen ring vibrations for different rings using PM3 [5] and HF/6-31G(d) [6,7] method. They were able to link characteristic bands in the IR spectra with normal modes calculated for

three, four and six-membered rings incorporated in cage-like structures.

In our earlier work [8], we used DFT together with B3-LYP/6-31G(d,p) method to investigate the conformation and vibrational spectra of aminopropylsilanetriol molecule (APST) which is the building block in aminopropylsiloxane polymer. The analysis of the low wavenumber Raman spectra of the same polymer [9] suggested ladder-like layered structure of medium range order.

In this work, we investigated IR and Raman spectra of aminopropylsiloxane (APS) polymerized on PVC substrate at room temperature. Complete assignment of the vibrational spectra was carried out using density functional theory calculations with Becke's three-parameter exchange functional in combination with the Lee–Young–Parr correlation functional (B3-LYP) and standard 6-311++ G(d,p) basis set. The vibrational spectra were calculated for two different conformations of silicoxygen rings: ladder structure (Fig. 1) and cubic structure (Fig. 2). Ladder structure with two rings was used to calculate structure and vibrational dynamics of APS (Fig. 3).

The dependence of geometrical parameters and vibrational frequencies on the number of subunits forming the

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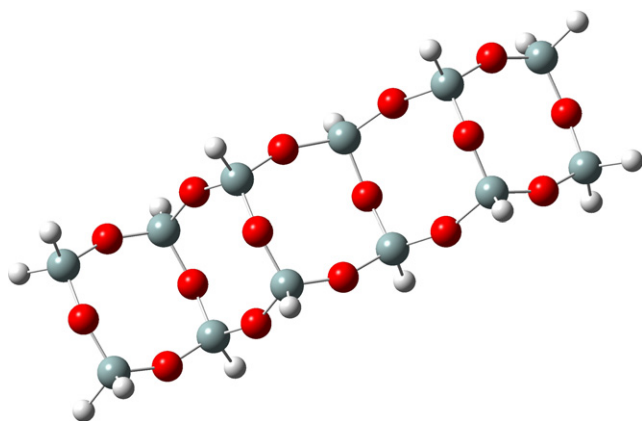


Fig. 1. Ladder structure.

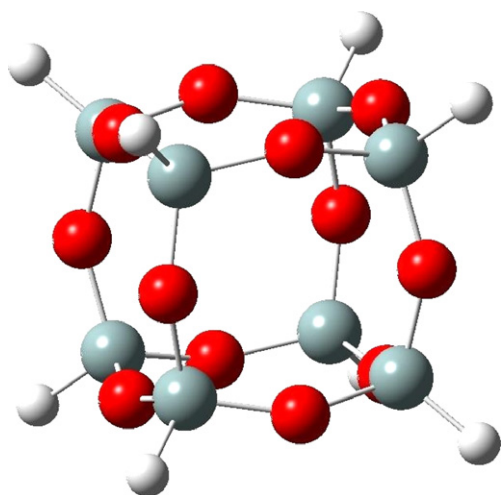


Fig. 2. Cubic structure.

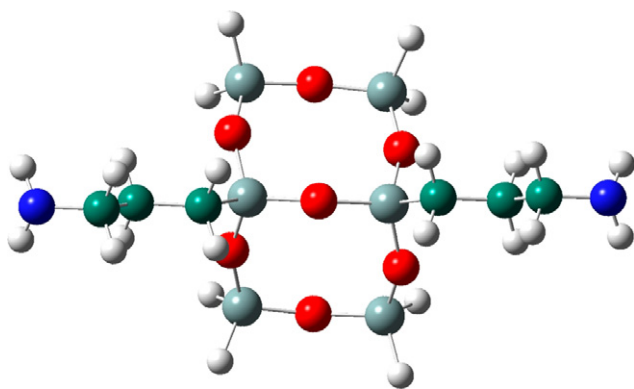


Fig. 3. Aminopropylsiloxane (APS).

ladder structure was also investigated. Because of the computational limitations we restricted our investigation to the eight-membered chain.

2. Experimental

Aqueous solution (25%) of aminopropylsilanetriol was purchased from ABCR Company. APS film about 1 mm thick was prepared by slow evaporation of water from the

solution deposited on PVC substrate. The film could be easily removed from the PVC support, showing that no chemical bonds were formed between APS and PVC.

The Raman spectra were recorded from 10 to 1700 cm^{-1} on a Dilor Model Z24 triple spectrometer using 514.5 nm argon ion laser excitation. Laser power at the sample was below 200 mW. The slit width was 600 μm corresponding to the spectral slit width of 5.76 cm^{-1} . 90° scattering geometry has been used. The incoming light was polarized vertically with respect to the scattering plane. The polarization of the scattered light was analyzed in vertical (VV) and horizontal (VH) direction (Fig. 4). The reorientation of the sample regarding the incident and scattered polarization did not make any difference in the Raman spectra.

The FT-IR spectra of APS were recorded in 400–1800 cm^{-1} spectral region, resolution being 4 cm^{-1} (Fig. 5). The spectra were obtained from KBr pellets using a Bruker Equinox 55 FT-IR spectrometer equipped with germanium diode as a detector and tungsten halogen lamp as a source.

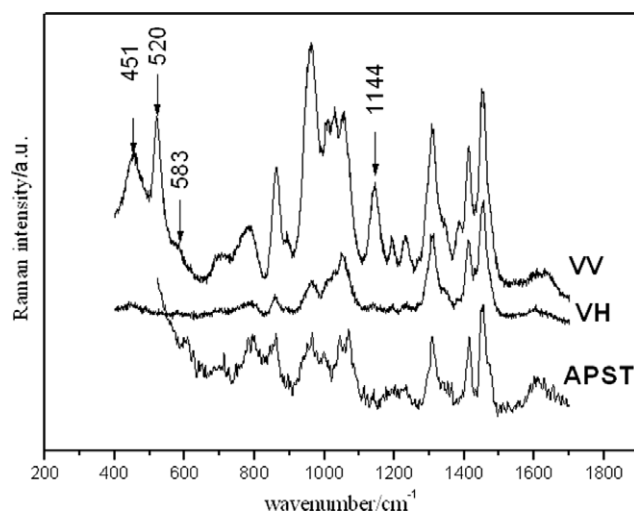


Fig. 4. Polarized Raman spectra of APS polymer and unpolarized Raman spectrum of APST water solution.

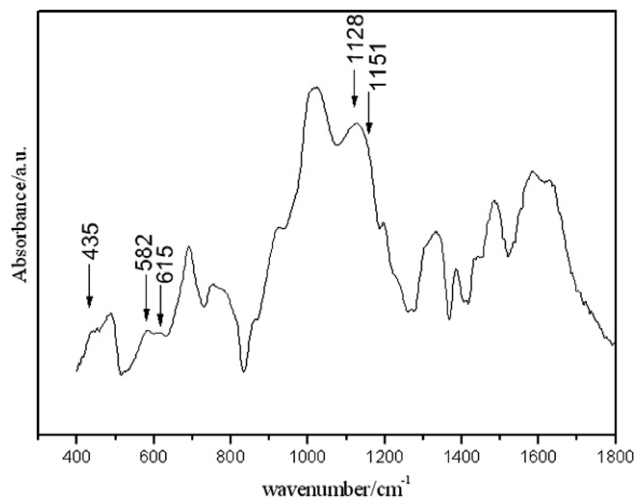


Fig. 5. IR spectrum of APS.

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