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Raman Analysis of Polymerization of APST Molecule

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Summary: In this work we investigated the solidification of aminopropylsilanetriol dissolved in water (~25%) under different conditions by Raman spectroscopy. The solidification was carried out at three different temperatures 8 °C, 23 °C and 60 °C. The influence of electromagnetic radiation on the polymerization process was also studied. Samples were held to solidify in dark and at UV (254 nm and 356nm) spectral range. In order to investigate the influence of the substrate on the resulting polymer structure, teflon, PVC, glass, brass and silica were used. Best ordered polymerized structure was achieved for samples deposited on plastics and solidified in dark, at room temperature.

Keywords: aminopropylsilanetriol; *gauche* conformers; ladder structure; polymerization; *trans*

Introduction

Organofunctional silanes act as an adhesion promoter between inorganic materials (glass, metal oxides or various fillers) and organic materials such as polymers.[1–4] They can improve mechanical properties, such as tensile strength, modulus of elasticity, moisture and corrosion resistance, etc.[5–8] Organosilanes have up to three hydrolysable groups which can react with hydroxylated surfaces forming Si$-$O$-$Si bonds. They can condense with each other as well, forming siloxane networks. Aminosilanes are widely used organosilanes. Aminopropylsilanetriol, APST ($NH_2-CH_3-CH_3-CH_3-Si-(OH)_3$) is a product of hydrolysis of aminopropylalkoxysilanes. Hydrolysis is followed by condensation process in which water molecules are released and siloxane linkages are formed.[9] These oligomeric chains can form different kinds of networks like ladder structures,[2] hydrogen bonded $SiOH\ldots NH_2$ network or zwitter-ionic $SiO^-\ldots H\ldots NH_2^+$ structure.[10] In this work, we investigated the influence of different polymerization conditions (temperature, electromagnetic radiation and substrate on which the solidification was going on) on the structure of the resulting polymer.

Experimental Part

25% aqueous solution of APST was purchased from ABCR Company. Polymer films about 1mm thick were prepared by slow evaporation of water from the solution deposited on different substrates. Influence of the substrate on which samples were deposited was examined for teflon, PVC, glass, brass and silica. During the polymerization process all these samples were held in dark at room temperature. In order to examine the influence of the temperature on the polymerization process, one sample was held in a refrigerator at constant temperature of 8 °C, second one was held at room temperature (23 °C), and third sample was heated at 60 °C in oven. All three samples polymerized at brass

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substrate. Influence of the electromagnetic radiation on polymerization was examined by exposing each of the three samples deposited on the PVC substrate to different radiation. One sample was held to polymerize in dark and the other two were illuminated by UV lamps (254 nm and 365 nm).

Raman spectra of polymerized samples from 1700 to 50 cm^{-1} were recorded on a Dilor Model Z24 triple monochromator coupled with an IBM AT computer. The green line (514.5 nm) of a Coherent INNOVA-100 Model argon ion laser was used as the excitation. The spectral resolution was 1 cm^{-1}. Although the polymerization process took place under different conditions, all the spectra were taken at room temperature.

Results and Discussion

APST molecule is stable only in aqueous solution, and if water from the solution starts to evaporate, polymerization process begins. Structures obtained under different conditions were analyzed by the Raman spectroscopy. Based on our previous work, density functional theory (DFT) analysis of molecular vibrations of APST[11] and aminopropylsiloxane polymer (APS),[12] we were able to find Raman bands characteristic for *trans* and *gauche* conformations of APST (Figure 1) as well as those corresponding to the formation of the Si–O–Si bonds in polymerized ladder structures (Figure 2, Table 1).

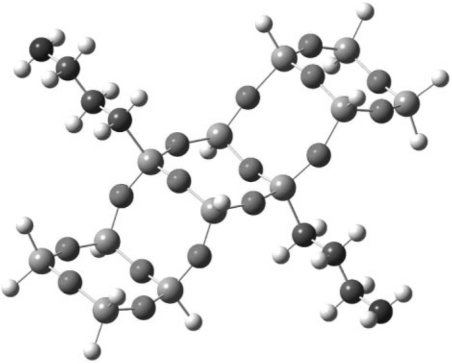

Figure 2.
Ladder structure of APS.

Table 1.
Characteristic vibrations of APST molecule and APS polymer.

ν_{exp}/cm^{-1}	ν_{calc}/cm^{-1}	assignment	structure
583	577	Si–O–Si str	ladder
615	615	Si–O–Si str	ladder
1050	1038	CH_2 twist, NH_2 rock	*trans*
1070	1064	CH_2 twist, NH_2 rock	*gauche*
1145	1137	Si–O–Si str	ladder

Influence of the Temperature

Raman spectra of samples polymerized at different temperatures are shown in Figure 3. Few bands sensitive to the temperature of polymerization can be distinguished. The intensity of the band observed at 1070 cm^{-1} is highest for the sample polymerized at 60 °C. This band looses its intensity as the temperature of the polymerization decreases. On the other hand, the band at 1050 cm^{-1}, almost invisible at 60 °C, gains the intensity when

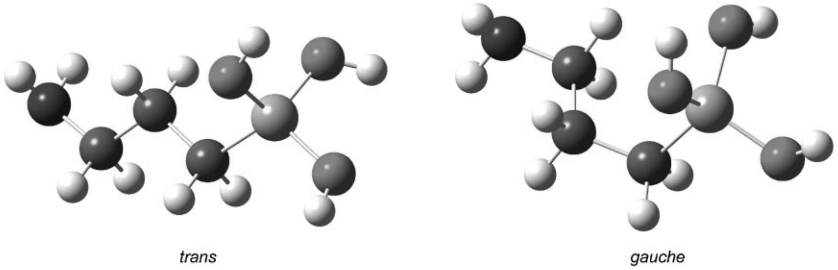

Figure 1.
Different conformations of APST.

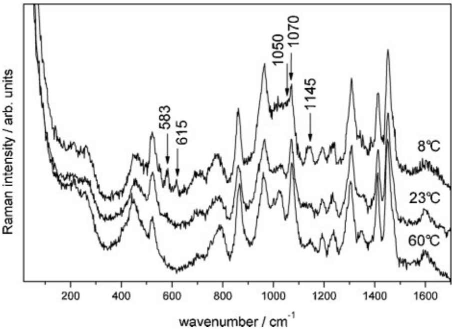

Figure 3.
Dependence of polymerization of APST on temperature.

the temperature is lowered. According to our DFT calculation of vibrational modes of APST molecule,[11] the bands at 1050 cm^{-1} and 1070 cm^{-1} correspond to the CH_2 twisting vibration coupled with NH_2 rocking in the propyl chains of *trans* and *gauche* conformers respectively (Table 1).

The observed changes in the intensity can be explained by the fact that *trans* and *gauche* conformers have different ground state energies (Table 2), the *trans* conformer being slightly more stable. There is increase in population of *gauche* conformer at the expense of *trans* one on heating the solution. On the other hand, intensity of the band characteristic for formation of Si−O−Si bond observed at 1145 cm^{-1} is decreasing with the temperature rise. This fundamental was assigned to the in phase Si−O−Si stretching in the rungs of the ladder structure. The other two bands at 583 and 615 cm^{-1} are out of phase and in phase Si−O−Si stretching alongside ladders, respectively.[10] The intensities of these bands also decrease at higher temperatures. This suggests that *trans* conformation favours the formation of ladder-like structures.

Table 2.
Conformer's and barrier transitions energies.[11]

	trans	*gauche*
Energy/eV	−18758.4878	−18758.4153
$\Delta E_{trans\text{-}gauche}$/eV	0.136	
$\Delta E_{gauche\text{-}gauche}$/eV	0.353	
$\Delta E_{gauche\text{-}trans}$/eV	0.054	

Influence of the Radiation

The spectra of structures solidified at different radiation wavelengths are presented in Figure 4. Spectra differ significantly only in the region of characteristic vibrational bands. Comparison of characteristic bands shows that by increasing the frequency of radiation, intensities of bands characteristic for *trans* conformer and Si−O−Si bond (Table 1) are decreasing, and those characteristic for *gauche* conformer is increasing. It seems that the radiation favours the formation of *gauche* structure, thus preventing building of ladders.

Influence of the Substrate

Influence of the substrate on the polymerization of silanes is shown on Figure 5. Thin films formed on teflon and PVC were easily removed, showing that there are no chemical bonds between polymerized samples and those two substrates. Samples placed on glass, brass and silica formed chemical bonds with their substrates. Substrate's morphology influences the process of polymerization. When silane does not form bonds with the substrate (like with teflon and PVC) or when the substrate is amorphous (like glass), spectra have band at 1145 cm^{-1}, which means that ladder structure is formed. If the substrate is

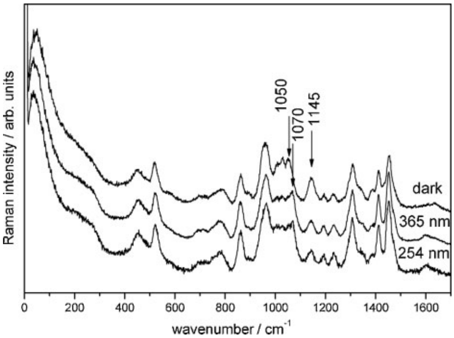

Figure 4.
Dependence of polymerization of APST on the wavelength of electromagnetic radiation.

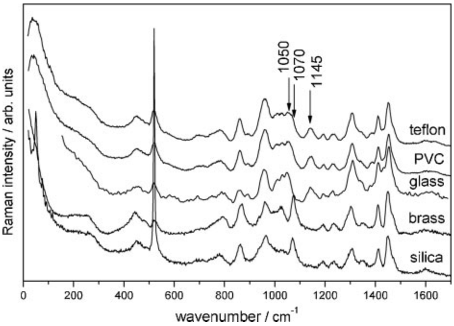

Figure 5.
Dependence of polymerization of APST on substrate.

crystalline (as silica or brass) there is no Si–O–Si band in the spectra, which means that ladder structure is absent. But those spectra have band at 1070 cm^{-1}, characteristic for *gauche* conformer. The possible explanation is in incommensurability of two periods: the ladder's and crystal substrate's. As is well known from the studies of Frenkel-Kontorova model,[13] the formation of incommensurate structures on periodic substrate is favorable at lower temperatures. We can relate this property with the fact that the portion of ladder structure is greater when solidification takes place at lower temperature (Figure 3).

Conclusion

Comparison of all those spectra shows that the best ordered polymerized structure have samples deposited on PVC substrate and solidified in dark, at room temperature, for about three weeks. In spectra of those samples only the bands of *trans* conformer were observed, and the Si–O–Si stretching band at 1145 cm^{-1} has the highest intensity. This conclusion is supported by the fact that in those spectra Bose peak can be easily observed at approximately 40 cm^{-1}. The analysis of the Bose band indicates the existence of the medium range ordered structure.[14]

Although the increase of the temperature and radiation speeds up the process of solidification, it decreases the formation of Si–O–Si bands, observed in spectra as low intensity of 1145 cm^{-1} band. By comparison of bands characteristic for *trans* and *gauche* conformers it can be observed that the intensity of the *gauche* band becomes larger when the temperature and the frequency of radiation are increasing. The possible explanation is that by increasing the temperature and radiation frequency, molecules are gaining energy, which is sufficient for overcoming the energy barrier for transition from *trans* to *gauche* conformer (Table 2).[11] Because of its' twisted structure, it is less likely for *gauche* conformer to form siloxane bonds.

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[1] M. J. Owen, in: "*Adhesion science and engineering 2: Surfaces, chemistry and applications*", M. Chaudhury, A. V. Pocius, Eds., Elsevier, Amsterdam 2002.

[2] Z. Demjén, B. Pukánszky, E. Földes, J. Nagy, *J. Colloid Interface Sci.* **1997**, *190*, 427.

[3] S. Lučić Blagojević, V. Kovačević, M. Leskovac, D. Vrsaljko, V. Volovšek, C. Nover, *E-polymers* **2004**, 036.

[4] P. Sae-oui, U. Thepsuwan, K. Hatthapanit, *Polym. Test.* **2004**, *23*, 397.

[5] A. N. Khramov, V. N. Balbyshev, N. N. Voevodin, M. S. Donley, *Prog. Org. Coat.* **2003**, *47*, 207.

[6] P. Cardiano, R. C. Ponterio, S. Lo Schiavo, P. Piraino, *Polymer* **2005**, *46*, 1857.

[7] M. Arroyo-Hernández, J. Pérez-Rigueiro, J. M. Martínez-Duart, *Materials Science and Engineering C* **2006**, *26*, 938.

[8] N. E. Cant, K. Critchley, H. L. Zhang, S. D. Evans, *Thin Solid Films* **2003**, *426*, 31.

[9] T. Ogasawara, A. Yoshino, H. Okabayashi, C. J. O'Connor, *Colloid Surf. A: Physicochem. Eng. Asp.* **2001**, *180*, 317.

[10] I. Shimizu, H. Okabayashi, K. Taga, E. Nishio, C. J. O'Connor, *Vibr. Spectrosc.* **1997**, *14*, 113.

[11] L. Bistričić, V. Volovšek, V. Dananić, I. Movre Šapić, *Spectrochim. Acta Part A* **2006**, *64*, 327.

[12] V. Volovšek, L. Bistričić, V. Dananić, I. Movre Šapić, *J. Mol. Struct.* **2007**, *834–836*, 414.

[13] O. M. Braun, Y. S. Kivshar, *Phys. Rep.* **1998**, *306*, 1.

[14] V. Volovšek, L. Bistričić, K. Furić, V. Dananić, I. Movre Šapić, *J. Phys.: Conference Series* **2006**, *28*, 135.