Temperature Dependence of Polarized Low Wavenumber Raman Spectra of Aminopropylsilanetriol Polymer

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Abstract. Low wavenumber polarized Raman spectra of aminopropylsilanetriol (APST) polymer deposited on PVC substrate were measured in the temperature range from 300 K to 78 K. In the low wavenumber Raman spectra of these samples a very strong Bose band was observed. The best results in modeling the low wavenumber Raman spectra were achieved with the exponential correlation function of disorder $G_{\text{dis}}(r) = \exp(-r/R_c)$ using three contributions: transversal and longitudinal acoustic phonons and molecular vibration. Results suggest medium range ordered ladder structure, stacked in layers with different orientations of ladders.

1. Introduction
Aminopropylsilanetriol (APST) is an organosilane coupling agent which can be adsorbed on different surfaces like optical fibers, nanoparticles, semiconducting or metal materials. These molecules are forming chemical bonds with the surface of substrate changing thus their mechanical, optical or electrical properties. The nature of the bonds between the APST and the substrate as well as the bonds between APST molecules depends greatly on the polymerization conditions. During condensation, silanol groups in different APST molecules are combining to form siloxane linkages, releasing water molecules in the process [1]. These oligomeric chains can form different kinds of networks like ladder structures [2], hydrogen bonded SiOH…NH₂ network or zwitter-ionic SiO⁻…H…NH₂⁺ structure [3].

Low wavenumber Raman spectra give valuable information about macromolecular structure and the relaxation processes in amorphous materials. In this work we used this technique in order to investigate the structure of polyAPST formed on PVC substrate.

2. Experimental
25% APST aqueous solution was purchased from ABCR Company. PolyAPST films around 1mm thick were prepared by slow evaporation of water from the solution deposited on PVC substrate. The films could be easily removed from the PVC support, showing that no chemical bonds were formed between APST and PVC. The sample was then cooled in a liquid nitrogen variable temperature cryo-
The samples were also examined between crossed polarizers. No light passed through the system when the light entered the sample perpendicular to the plane of growth. When the sample was turned by 90° so that the light was entering parallel to the plane of growth (through the thin side of the sample), maximum intensity of transmitted light was detected for the sample oriented diagonally between crossed polarizers. This is the indication that there exists optical anisotropy in the polymer although it could not be detected in polarized Raman spectra.

3. Results and discussion
The Raman spectra of APST polymer film comprise a characteristic boson peak (BP), a broad asymmetric continuous band placed between 20 and 200 cm⁻¹. According to the model of Martin and Brenig (MB) [4] boson peak represents acoustic modes of sample becoming active in Raman spectrum due to the break-down of selection rules in amorphous materials.

It is well established that the low wavenumber Raman spectrum of amorphous media can be partitioned into three contributions [5]:

\[ I_{\text{exp}}(\nu) = I_{\text{QE}}(\nu) + I_{B}(\nu) + I_{V}(\nu) \]

where \( I_{\text{QE}}(\nu) \) is quasi-elastic scattering, \( I_{B}(\nu) \) boson peak and \( I_{V}(\nu) \) low wavenumber vibrational modes. It is convenient to use redefined Raman intensity:
\[ I_R(v) = I_{\text{exp}}(v) \cdot n(v, T) + 1 = I_{ROE}(v) + I_{RB}(v) + I_{RV}(v), \]
\[ n(v, T) = \exp\left(\frac{hc \nu}{k_B T}\right) - 1 \] is a temperature Bose factor.

Following the approach to the description of redefined Raman intensity in the region where the contribution of quasi-elastic scattering is negligible \((\alpha \geq 10 \text{ cm}^{-1})\), \(I_{RB}(v)\) can be factorized:
\[ I_{RB}(v) = C(v) \cdot g(v). \]
\(C(v)\) is light-vibration coupling coefficient and \(g(v)\) is the density of vibrational states.

In the MB model the vibrational density of states of acoustic phonons is Debye-like: \(g(v) \propto v^2\). The model considers spatial fluctuations of the wave vector \(q\) of the transversal (TA) and longitudinal (LA) acoustic phonons as well as the dielectric properties of disordered medium. This implies that the dominating origin of boson peak is the photon-phonon coupling coefficient:
\[ C(v) = v^2 \cdot g_{TA}(v) \cdot E_{TA} + g_{LA}(v) \cdot E_{LA}. \]

According to Malinovsky and Sokolov [6] several forms of \(g_i(v)\) are physically acceptable. In the case of APST polymer film the overall spectrum is Lorentzian-like and the model with the exponential correlation function of disorder \(G_{dis}(\nu) = \exp(-\nu/R_c)\) gives the best results in the modeling of BP. \(R_c\) is so-called structure correlation radius. This type of disorder gives:
\[ g_{TA}(v) = \left(\nu^2 + v_{TA}^2\right)^{-2} \]
\[ g_{LA}(v) = \left(\nu_{TA}^2 / \nu_{LA}^2\right)^{5} \cdot \left(\nu^2 + v_{LA}^2\right)^{-2}. \]

The reduced Raman intensity \(I_{\text{REDexp}}(v) = I_R(v)/v^2\) was calculated using experimental Raman spectrum \(I_{\text{exp}}(v)\). The following expression for reduced Raman \(I_{\text{REDcalc}}(v)\) intensity was used for data modeling:
\[ I_{\text{REDcalc}}(v) = \frac{I_R(v)}{v^2} = I_0 + \frac{v^2 \cdot E_{TA}}{\left(\nu^2 + v_{TA}^2\right)^{5}} + \nu \cdot \frac{(\Gamma_{v} / 2)^2}{(\nu - \nu_{v})^2 + (\Gamma_{v} / 2)^2} \cdot \frac{1 - \exp(hc \nu / k_B T)}{v}. \]

The intensity of QE scattering tends to zero at a wavenumber \(\nu \geq 15 \text{ cm}^{-1}\) and it is neglected in the model function. The background noise in Raman spectra \(I_0\) has been taken into account in modeling as a free parameter. The molecular low wavenumber vibrational band in Raman spectra \(I_0\) is Lorentzian \(I_V \cdot (\Gamma_{v} / 2)^2 / (\nu - \nu_{v})^2 + (\Gamma_{v} / 2)^2\). The model parameters were estimated through least-squares fit to the observed spectral amplitudes with uncertainties calculated according to the actual photon count. The model depends on eight parameters, of which in four it is non-linear. The best fit parameter values are derived by iterative optimization routine, followed by the Jackknife procedure to estimate the parameter uncertainties [7]. The model is tested by calculated goodness of fit G or reduced chi-square \(\chi_r^2\) test. It is common to accept the model with \(G > 0.001\), or with \(\chi_r^2 < 1.5\) [5].

Best fit parameter values and corresponding uncertainties are shown in Table 1. The reduced chi-square \(\chi_r^2 = 0.21\) and goodness of fit \(G = 1\) was obtained. The results of the fitting of reduced Raman intensity are shown in Table 1. and Fig. 2.

Table 1. Boson and vibrational contributions to the reduced low-wavenumber Raman spectra

| T (K) | \(I_0 \pm \sigma_0\) (arb.units) | \(E_{TA} \pm \sigma_{E_{TA}}\) (arb.units) | \(\nu_{TA} \pm \sigma_{\nu_{TA}}\) (cm\(^{-1}\)) | \(E_{LA} \pm \sigma_{E_{LA}}\) (arb.units) | \(\nu_{LA} \pm \sigma_{\nu_{LA}}\) (cm\(^{-1}\)) | \(I_v \pm \sigma_{I_v}\) (arb.units) | \(\nu_v \pm \sigma_{\nu_v}\) (cm\(^{-1}\)) | \(\Gamma_v \pm \sigma_{\Gamma_v}\) (cm\(^{-1}\)) |
|-------|-------------------------------|---------------------------------|---------------------------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|-------------------------------|
| 300   | 0.937 ± 0.042                 | 146287 ± 815                  | 55.19 ± 0.36                    | 14.12 ± 0.30                  | 58.18 ± 12.07                  | 206.48 ± 1.17                 | 132.89 ± 7.36                  |  |
According to the DFT calculation the broad Lorentzian band at 206 cm\(^{-1}\) consists of several contributions originated in the vibrational deformations of the propyl groups.

Apart from the portion of the spectrum analyzed by the fitting procedure, in the VV spectra of the sample there exist two pronounced vibrational bands at 454 cm\(^{-1}\) and 522 cm\(^{-1}\). The DFT calculation of the ladder structure attributes the first one to the breathing mode of the Si-O-Si ring, while the second one is the quadrupolar mode of the same group of atoms. Both bands are totally polarized.

The existence of BP in the low wavenumber Raman spectra reveals the persistence of medium range order in disordered polyAPST down to 78 K. On the other hand, the optical anisotropy of the sample as well as polarized vibrational bands at 454 cm\(^{-1}\) and 522 cm\(^{-1}\) would suggest ladder-like layered structure oriented parallel to the plane of growth. Thickness of the layers, orientation of ladders in different layers, as well as their lengths could be the origin of disorder.

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