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The Structure of Aminopropylsiloxane Polymerized in DC Electric Field

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Summary: The Raman spectra of aminopropylsiloxane (APS) polymerized on PVC substrate in DC electric field were measured to study the structure of deposited films. The modelling of low wavenumber Raman spectra was achieved using contribution of acoustic phonons, intramolecular vibrations as well as optical phonons related to librational motions of ladders. Results suggest that electric field influences the orientations of ladders increasing thus the degree of order in microdomains.

Keywords: acoustical phonons; aminopropylsiloxane; bose peak; DC electric field; libration

Introduction

Aminopropylsilanetriol (APST) is frequently used as a coupling agent for functionalization of surfaces like semiconductors, nanopariticles, optical fibres etc. The molecules of APST are metastable units which undergo self-condensation to thermodynamically more stable units with Si–O–Si siloxane bonds by elimination of water. The bonding of APST with the surface of substrate depends on the conformation of polymerized structure. Controlled hydrolysis of aminopropylsiloxane polymer (APS) provides polysiloxanes with different structures.

Recently, we have investigated the vibrational dynamics and structure of APS polymer using DFT calculations.[1] The analysis of low wavenumber polarized Raman spectra of APS polymerized on PVC substrate suggests medium range ordered ladder structure, stacked in layers with different orientation of ladders.[2] Ladder polymers are of particular interest in the field of advanced materials due its incontestable superiority in thermo- or radiation-resistant and mechanical properties.[3] The synthesis of structure-controlled ladder polymers has been a challenge in the polymer research field.

According to DFT calculations APST molecule has permanent electric dipole moment.[4] When the DC electric field is applied to polar molecules, the dipoles tend to orient themselves along the direction of the field. Therefore, the polymerization in electric field is considered a useful method to control the molecular orientation in polymers.[5–8]

In this work we investigated the structure of APS polymerized on PVC substrate in DC electric field. The study of Raman scattering from intramolecular and intermolecular modes in APS films was thus performed to obtain the information regarding polymer structure.

Experimental Part

Aminopropylsilanetriol (APST) in 25% aqueous solution was purchased from ABCR Company. APS polymer films around 1 mm thick were prepared by deposition of APST aqueous solution on PVC substrate. The condensation process was going on very slow. The condensation was carried out at room temperature in dark for approximately four days. The polymerization in electric field was carried out on PVC

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substrate that is laid between two metal plates of condenser linked up with high voltage DC power. The electric field intensity in range 10^3–$3.5 \cdot 10^5$ V/m was obtained by adjusting the output voltage in high voltage DC power as well as the distance between the plates.

The Raman spectra of APS from 3500–10 cm^{-1} were recorded on a Dilor Model Z24 triple monochromator coupled with an IBM AT computer. The 514.5 nm line of a Coherent INNOVA-400 argon ion laser was used for excitation. Laser power at the sample was below 200 mW. The spectral resolution was 2 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.

Results and Discussion

The Raman spectra of APS polymerized in various electric field intensities are compared in Figure 1. The intensity of each spectrum is normalised to the peak intensity of the 1452 cm^{-1} band assigned to the CH_2 scissoring vibrations. It can be noted that there are no significant difference among those spectra in the frequency region above 300 cm^{-1}. All spectra comprise the characteristic vibrations of ladder APS polymer observed at 1144, 520 and 451 cm^{-1}.[1] According to our normal mode analysis based on DFT calculations the band at 1144 cm^{-1} is assigned as in phase Si-O-Si stretching vibrations in the rungs of the ladder structures.[1] The fundamental at 520 cm^{-1} can be described as the ring breathing mode of silicon atoms, while those observed at 451 cm^{-1} corresponds to the ring breathing mode of oxygen atoms.[1]

The low frequency Raman spectra of all samples are dominated by very strong Bose band.

Our previous analysis has shown that the low wavenumber Raman spectra of APS polymerized on PVC substrate without electric field consist of two contributions: a broad vibrational band centred around 200 cm^{-1} and very strong Bose band with

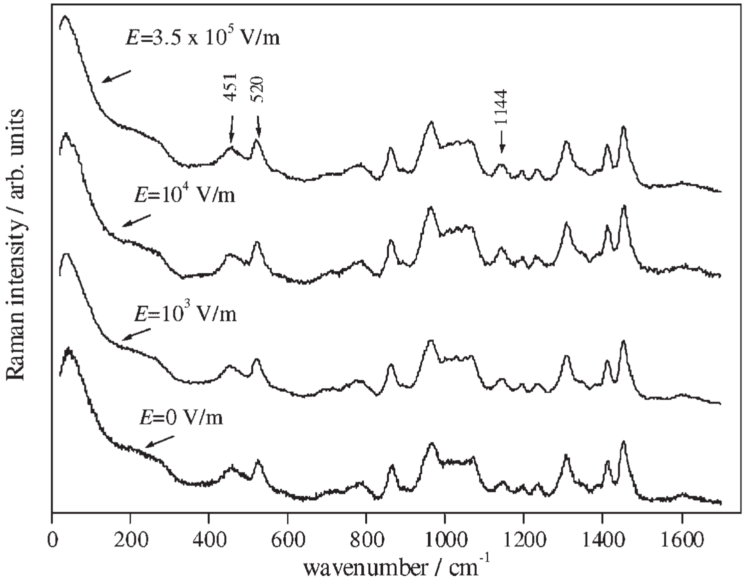

Figure 1.

Raman spectra of APS polymerized in different electric field intensities. The intensity of each spectrum is normalised by the peak height of the 1452 cm^{-1} intramolecular band.

maximum measured at 42 cm^{-1}.[2] The broad vibrational band consists from contribution of normal modes related to the quadripolar mode of silicooxygen rings as well as to deformations of propyl groups.[1] The contribution of intramolecular vibrations in the frequency region below 100 cm^{-1} can be neglected because DFT calculations predict very low Raman activity for those modes.[1]

We have shown that the nature of Bose band in APS polymerized on PVC substrate without electric field can be explained by model elaborated by Martin and Brenig[9] and then modified by Malinovsky and Sokolov[10] (MB model). According to this model, Bose band has been closely related to the acoustic transversal (TA) and longitudinal (LA) phonons in the medium range ordered structure. The medium range order implies that the arrangements of structural units are not completely random but have some correlation.[11]

It is well established that the observed low frequency Raman spectrum of disordered materials consists from quasi-elastic scattering $I_{QE}(\nu)$, Bose peak $I_B(\nu)$ and low-frequency vibrational modes $I_V(\nu)$:[2]

$$I_{\exp}(\nu) = I_{QE}(\nu) + I_B(\nu) + I_V(\nu). \tag{1}$$

It is usual to define the reduced Raman intensity:

$$\begin{aligned} I_R(\nu) &= I_{\exp}(\nu) \cdot \nu \cdot [n(\nu, T) + 1]^{-1} \\ &= I_{RQE}(\nu) + I_{RB}(\nu) + I_{RV}(\nu), \end{aligned} \tag{2}$$

where $n(\nu, T) = [\exp(hc\nu/k_B T) - 1]^{-1}$ is a temperature Bose factor.

For easier comparison with various theoretical models we used another expression for the reduced Raman intensities:

$$I_{RED\exp}(\nu) = \frac{I_R(\nu)}{\nu^2} \tag{3}$$

$I_{RED\exp}(\nu)$ was calculated according relations (2) and (3) using experimental Raman spectrum $I_{VH}(\nu)$ normalised by the peak height of the 1452 cm^{-1} band. Our aim was to fit particular model to an observed spectrum $I_{RED\exp}(\nu)$.

In MB model, in the region $\nu \geq 10$ cm^{-1} where the quasi-elastic light scattering is negligible, the redefined intensity of Bose band $I_{RB}(\nu)$ can be factorized:

$$I_{RB}(\nu) = C(\nu) \cdot g(\nu). \tag{4}$$

The well known Debye expression $g(\nu) \propto \nu^2$ is used for the density of states of acoustic phonons. $C(\nu)$ describes the coupling between the light and vibrational modes:

$$C(\nu) = \nu^2 \cdot [g_{TA}(\nu) \cdot E_{TA} + g_{LA}(\nu) \cdot E_{LA}], \tag{5}$$

where $g_i(\nu)$ is space Fourier transforms of the correlation function of disorder and E_i is light-vibration coupling parameters for transversal and longitudinal acoustic phonons. The best results in modelling the Bose band was achieved with exponential correlation function of disorder $G_{dis}(\nu) = \exp(-r/R_c)$, ($R_c$ is so-called structure correlation radius), which leads to:

$$\begin{aligned} g_{TA}(\nu) &= \left(\nu^2 + \nu_{TA}^2\right)^{-2} \text{ and } g_{LA}(\nu) \\ &= (\nu_{TA}/\nu_{LA})^5 \cdot \left(\nu^2 + \nu_{LA}^2\right)^{-2}, \end{aligned} \tag{6}$$

where $\nu_i = c_i/\pi \cdot R_c$ and c_i is respective (TA) or (LA) sound velocity. Such function of disorder corresponds to the structure of continuous network, which consists of the ordered microregions of the size $\sim 2\ R_c$.[10]

The model function $I_{REDcalc}(\nu)_{E=0}$ for fitting the reduced Raman spectra has been defined as:

$$\begin{aligned} I_{REDcalc}(\nu)_{E=0} = I_0 + C(\nu) \\ + I_V \frac{(\Gamma_V/2)^2}{(\nu - \nu_V)^2 + (\Gamma_V/2)^2} \\ \cdot \frac{1 - \exp(hc\nu/k_B T)}{\nu} \end{aligned} \tag{7}$$

The background noise in Raman spectra I_0 has been taken into account in modeling as a free parameter. The molecular low-frequency vibrational band in Raman spectra is presented with Lorentzian $I_V(\Gamma_V/2)^2/\left((\nu - \nu_V)^2 + (\Gamma_V/2)^2\right)$.

In the Raman spectra of all samples polymerized in electric field the maximum

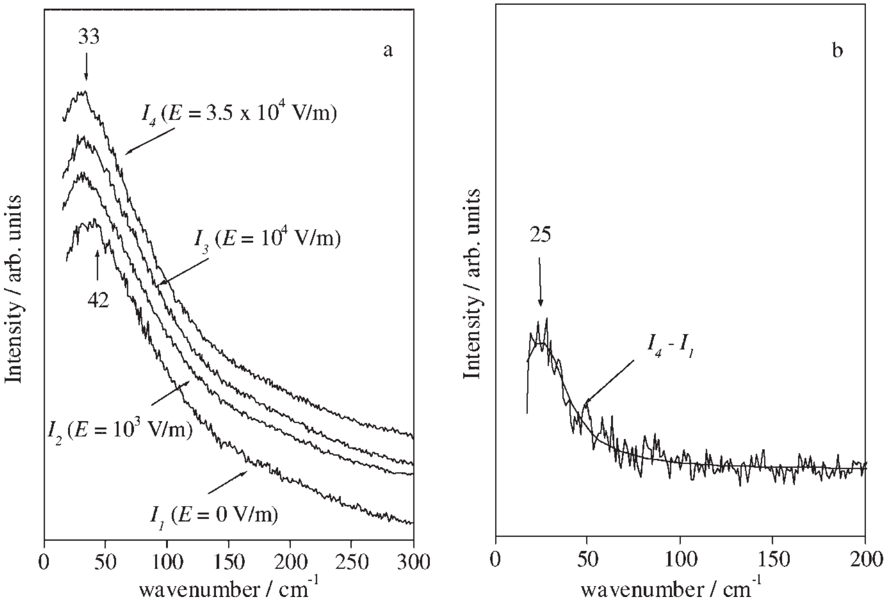

Figure 2.
a) The reduced I_{VH} Raman spectra for different intensities of electric field; b) The difference Raman spectrum fitted to the Lorentzian band.

of Bose band is shifted to 33 cm^{-1}. The model function represented with relation (7) could not reproduce the observed reduced low frequency I_{VH} Raman spectra (Figure 2a). In an attempt to solve this problem we took the difference spectra between the reduced Raman intensities of the samples polymerized in various intensities of electric field and without electric field. All these spectra show the Lorentzian band centred at around 25 cm^{-1} (Figure 2b). Therefore, we included the additional vibrational band to the model function. The following expression for reduced Raman intensity $I_{REDcalc}(\nu)_{E\neq 0}$ was used for data modeling:

$$I_{REDcalc}(\nu)_{E\neq 0} = I_{REDcalc}(\nu)_{E=0} + I_L \frac{(\Gamma_L/2)^2}{(\nu-\nu_L)^2+(\Gamma_L/2)^2} \cdot \frac{1-\exp(hc\nu/k_BT)}{\nu} \tag{8}$$

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 eleven parameters. In six of them 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.[12] The model is tested by calculated goodness of fit G. It is common to accept the model with $G > 0.001$.[12] Best fit parameter values, corresponding uncertainties and goodness of fit G are given in Table 1. The results of the fitting of reduced Raman intensity for APS polymerized in electric field 10^3 V/m are shown in Figure 3a.

As can be seen from the results in Table 1 and Figure 3a the main contribution to the Bose band arises from transversal acoustic phonons TA. The frequency ν_{TA} of transversal acoustic phonons in disordered media lies between 10–80 cm^{-1} and depends on chemical composition, pressure as well as thermal history of the sample.[10] In the reduced Raman spectra of APS the position of $\nu_{TA} \sim 50$ cm^{-1} and the value of coupling

Table 1.
Bose, vibrational and librational contribution to the reduced low-wavenumber Raman spectra in dependence on electric field intensity.

$E^{a)}$	0	10^3	10^4	$3.5 \cdot 10^5$
$I_o \pm \sigma_{Io}$	111.50 ± 7.58	212.54 ± 3.04	238.94 ± 4.37	146.14 ± 3.78
$E_{TA} \pm \sigma_{ETA}$	144.14 ± 1.97	143.78 ± 1.64	150.06 ± 2.16	144.46 ± 2.80
$\nu_{TA} \pm \sigma_{\nu TA}$	51.30 ± 1.24	50.54 ± 0.57	49.96 ± 0.62	48.55 ± 0.62
$E_{LA} \pm \sigma_{ELA}$	71.28 ± 36.62	0.86 ± 0.68	1.95 ± 0.17	6.00 ± 0.52
$\nu_{LA} \pm \sigma_{\nu LA}$	17.83 ± 1.46	9.21 ± 1.15	10.21 ± 1.32	11.65 ± 1.27
$I_V \pm \sigma_{IV}$	321.36 ± 30.72	213.20 ± 9.48	277.95 ± 15.00	240.80 ± 13.74
$\nu_V \pm \sigma_{\nu V}$	200.10 ± 2.65	197.23 ± 1.38	198.44 ± 1.56	195.45 ± 1.79
$\Gamma_V \pm \sigma_{\Gamma V}$	143.85 ± 18.66	98.67 ± 7.74	120.94 ± 9.49	119.45 ± 10.98
$I_L \pm \sigma_{LV}$	–	929.92 ± 200.00	658.40 ± 247.50	550.20 ± 292.00
$\nu_L \pm \sigma_{\nu L}$	–	$26.\ 77 \pm 1.42$	28.02 ± 2.21	28.18 ± 8.00
$\Gamma_L \pm \sigma_{\Gamma L}$	–	32.76 ± 3.80	29.03 ± 5.37	27.18 ± 2.60
G	0.140	0.176	0.305	0.010

a)(E in V/m; $I_o \cdot 10^{-5}$, $\sigma_{Io} \cdot 10^{-5}$, E_{TA}, σ_{ETA}, $E_{LA} \cdot 10^{-3}$, $\sigma_{ELA} \cdot 10^{-3}$, $I_V \cdot 10^{-3}$, $\sigma_{IV} \cdot 10^{-3}$, $I_L \cdot 10^{-3}$, $\sigma_{LV} \cdot 10^{-3}$ in arb. units; ν_{TA}, $\sigma_{\nu TA}$, ν_{LA}, $\sigma_{\nu LA}$, ν_V, $\sigma_{\nu V}$, Γ_V, $\sigma_{\Gamma V}$, ν_L, $\sigma_{\nu L}$, Γ_L, $\sigma_{\Gamma L}$ in cm^{-1}).

coefficient E_{TA} are independent of electric field. The frequency of longitudinal acoustic mode in sample polymerized without electric field is calculated at 17.83 cm^{-1}.

The frequencies of longitudinal modes in samples polymerized in electric field moves towards lower values and are in the range 9.21–11.65 cm^{-1}. The coupling coefficient E_{LA} has the greatest value without electric field, and significantly decreases in electric field. It is important to emphasise that the contribution of longitudinal acoustic phonon to the Bose band is dominated with position of ν_{LA} (relations 5. and 6.) and not with E_{LA}. Consequently, in spite of the significant decrease of E_{LA} in the electric field the contribution of LA phonon remains important (Figure 3b).

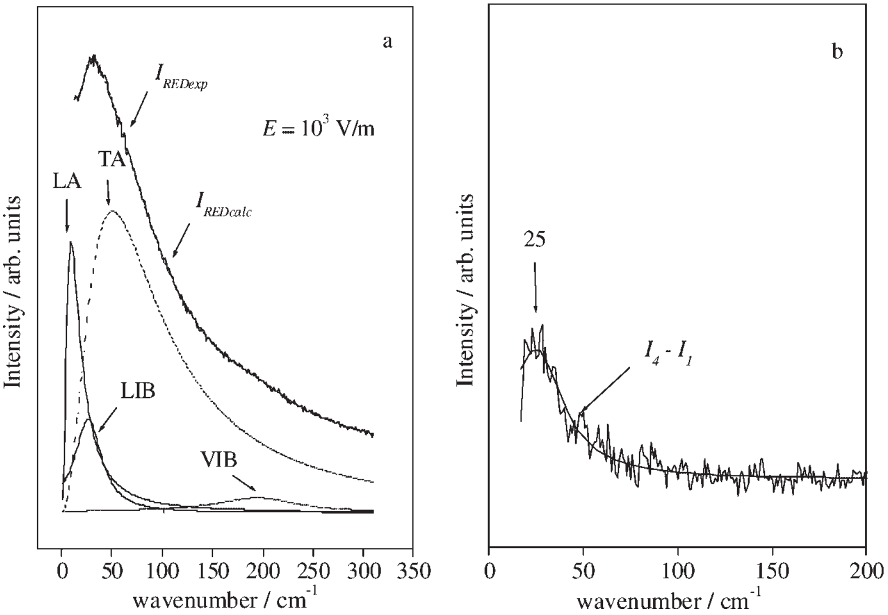

Figure 3.
a) Results of fitting of the reduced Raman intensity at $E = 10^3$ V/m (LA-longitudinal acoustic phonons; TA-transversal acoustic phonons; LIB-librational contribution; VIB-vibrational contribution); b) The dependence of longitudinal acoustic phonons LA on electric field intensity.

The similar results are obtained in studies that analyze the influence of pressure on fast dynamics and elastic properties of different materials including polymers.[13] The variations of TA modes under pressure are significantly smaller than that of LA modes. Detailed studies of disordered materials demonstrated that variation in Bose peak frequency under pressure is stronger than the variation in the sound velocity.[13] The size of ordered microdomains, or the structural correlation range can be estimated from the position of acoustic phonons and the sound velocity. Assuming that the velocity of longitudinal acoustic wave in APS samples changes slower than the frequency ν_{LA}, the structure correlation radius R_c increases in samples polymerized in electric field. In that case the dimensions of ordered domains in longitudinal direction are greater.

The Bose band can also be analysed using the depolarization ratio of the recorded low frequency Raman spectra. According MB model disorder-induced Raman scattering is ascribed to the electrical and mechanical disorder. As shown by Novikov *at al.*,[14] the strain tensor can be divided into diagonal and traceless parts. The traceless tensor is responsible for the depolarized Raman intensity I_{VH} and for part of the polarized Raman intensity $\mathrm{I_{VV}}$; the diagonal tensor is responsible for the polarised intensity I_{VV}. The depolarization ratio $\rho = I_{VH}/I_{VV}$ is equal to 0.75 or 0, according to whether transversal or longitudinal modes, respectively, produce the scattering. Obviously, ρ lies between these limits if both kinds of modes scatter. The depolarization ratio of Bose band in all APS samples in range 0.50–0.56 also indicates the transverse-like character of acoustic vibration contributing to the spectra in the low frequency region.

The conformational and vibrational analysis of APST molecule has shown that there are two stabile conformers *trans* and *gauche*.[4] The *trans* conformer is the predominant form present in APS polymer. The calculated dipole moment of *trans* APST molecule is $6.86 \cdot 10^{-30}$ Cm. Therefore, the electric field-induced orientation of aminopropyl segments during polymerization is expected. The analysis and the modeling of low frequency Raman spectra confirmed the existence of vibrational band at $\sim$28 cm^{-1} (Table 1 and Figure 2b). According to the general principle that in the Raman scattering the intensities of rotatory fundamentals are always much stronger than those of translatory motions, the observed band probably arises due to the librational motions of ladders.[15]

Conclusion

The Raman light scattering study has been undertaken to elucidate the structure of APS polymerized in DC electric field. The analysis shows that applied electric field has no influence on the intramolecular vibrations. The changes are pronounced in the low wavenumber region. The low frequency Raman spectra consist from Bose band, optical phonons and intramolecular vibrations. The modelling of Bose band has shown the shift of longitudinal acoustical phonons toward lower frequencies as well as a possible enhancement of structure correlation radius R_c. The observed optical phonon centred around 28 cm^{-1} due to the libration of ladders suggests the orientational ordering in microdomains.

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