



Raman Spectra of Poly[di-*n*-propylsilylene]s and σ - σ Conjugation

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σ - σ -Conjugation in polysilylenes manifests itself in the Raman spectra qualitatively in a similar way to π - π -conjugation in polyenes, leading to a significant enhancement of lines corresponding to the stretching vibrations of the bonds participating in conjugation.

It is well-established that conjugation of bonds in organic molecules leads to a significant enhancement of the intensity of Raman lines corresponding to the stretching vibrations of the bonds participating in conjugation.¹ It was first demonstrated in the early forties by Shorygin and Volkenstein on examples of compounds containing conjugated C=C and C=O π -bonds. For polyene molecules, the elongation of a conjugated chain by one more C=C double bond leads to an approximately ten-fold

increase in the Raman intensity of the corresponding line (in the cited cases the spectra were excited by the 4358 Å Hg line).^{2,3}

A theory was developed^{1,4,5} to explain the enhancement of Raman line intensity in the spectra of conjugated compounds by the following factors: i, resonance enhancement as the frequency of the irradiating light approaches the frequency of the molecular transition to the excited level, 'actual' for Raman scattering; ii, an increase in the shift of the equilibrium position δ_i

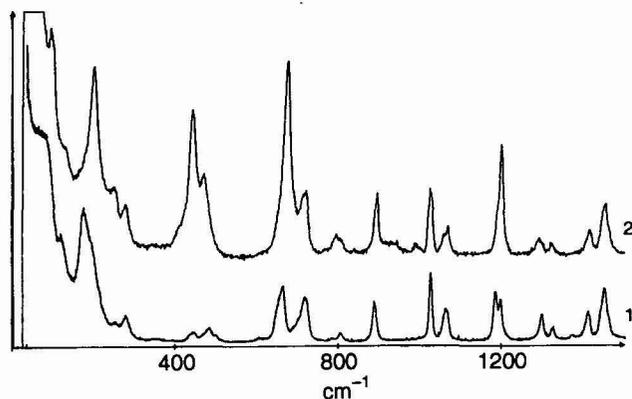


Fig. 1 Comparison of the Raman spectra of solid samples of $[\text{Pr}_2\text{Si}]_5$ (1) and $[\text{Pr}_2\text{Si}]_n$ (2) obtained at room temperature with 5145 Å excitation.

of an i -th vibrational mode upon electronic excitation of the molecule; iii, an increase in the constant η_i of vibronic coupling, leading to a dependence of electronic transition dipoles on nuclear vibrational coordinates.

In recent years much attention has been paid to the study of poly[dialkylsilylene]s—molecules containing only silicon atoms in the backbone and only σ -bonds between all the atoms.⁶ These compounds exhibit some properties analogous to those of conjugated polyenes; for this reason polysilylenes are considered as σ - σ conjugated systems with delocalization of the Si-Si σ -electrons.⁷ It is interesting to examine the Raman intensity behaviour of poly[dialkylsilylene]s in order to reveal similarities and differences in the manifestation of π - π and σ - σ conjugation in the Raman spectra.

With this in mind, we have undertaken experimental and theoretical studies of various polysilylenes. Here we report the Raman spectra of a σ - σ conjugated high-molecular weight polymer, $[\text{n-Pr}_2\text{Si}]_n$, and for comparison of a low-molecular weight ring, $[\text{n-Pr}_2\text{Si}]_5$, both compounds having the same composition. The dependence of the Raman spectra on the wavelength of the exciting laser line was also investigated.[†]

The polymer was shown to have an all-*trans* planar structure, favouring maximum σ - σ conjugation.^{8,9} In the $[\text{n-Pr}_2\text{Si}]_5$ ring the conditions for conjugation should be much less favourable.

The Raman spectra of both compounds in the region 5–1600 cm^{-1} are compared in Fig. 1. Both spectra were excited by the 5145 Å line of an Ar^+ laser. The vibrational spectrum of the polymer along with the band assignment was published

[†] Experimental. The Raman spectra were obtained using RAMANOR-HG2S and U-1000 laser Raman spectrometers. ILA-120 Ar^+ , ILK-120 Ar-Kr^+ and SP-124 He-Ne lasers were used for exciting the spectra. Laser power applied was not more than 100 mW to avoid photo-dissociation. The solid samples were sealed *in vacuo* in glass capillaries. No special wavelength-dependent intensity corrections were made, but the spectra, excited by different wavelengths, were normalized so as to make the intensities of the $\delta(\text{C-H})$ lines in the region 1450 cm^{-1} approximately equal.

Poly[di-*n*-propylsilylene] was prepared by sodium coupling of $\text{n-Pr}_2\text{SiCl}_2$ in toluene at 110 °C, in the usual way;⁶ the preparation will be reported in more detail elsewhere.⁹

Deca-*n*-propylcyclopentasilane was synthesized as follows: lithium (4.0 g, 0.5 mol) was cut into small pieces and added to 400 ml of THF containing 0.5 g of hexaphenyldisilane as equilibration catalyst.²¹ Under nitrogen, a solution of 46.4 g (0.25 mol) of $\text{n-Pr}_2\text{SiCl}_2$ (Huls) in 100 ml of THF was added with stirring at 0 °C. 300 ml of cyclohexane was added and the mixture was filtered to remove LiCl. The solution was evaporated to 200 ml, then 100 ml of hexane was added and the solution was washed with two 200 ml portions of water. Evaporation of the dried solution gave a white solid, which was recrystallized from ethanol giving 18 g (61%) of $(\text{n-Pr}_2\text{Si})_5$, 95% pure according to GPC. Final purification was accomplished by reversed-phase HPLC on an octadecylsilane-treated silica column, eluting with THF-methanol. (Found: C, 63.07; H, 12.35. Calc. for $\text{C}_{30}\text{H}_{70}\text{Si}_5$: C, 62.94; H, 12.40%); λ_{max} (hexane) 260 nm.

recently.⁹ The assigned Raman spectra of silicon five-membered rings, but with substituents other than *n*-Pr, can be found in refs. 10–12.

It is seen from Fig. 1 that spectra are very much alike, especially in the region of 800–1600 cm^{-1} where the bands corresponding to the internal vibrations of propyl groups are situated. However, there is a striking difference between the two spectra; the relative intensity of the symmetric skeleton stretching vibrations $\nu^s(\text{Si-Si})$ at ca. 450 cm^{-1} and $\nu^s(\text{Si-C})$ at ca. 670 cm^{-1} is greatly enhanced in the spectrum of the polymer.[†]

Thus, it can be concluded that σ - σ conjugation in polysilanes affects the Raman scattering qualitatively in the same way as π - π conjugation in polyenes, both phenomena leading to an increase in intensity of the lines corresponding to the symmetrical stretching vibrations of conjugated bonds.

However, the increase in the intensity of the $\nu^s(\text{Si-C})$ line, which dominates in the spectrum of the polymer, is not a trivial result and calls for further investigations. This finding is in agreement with the earlier proposal that the Si-C σ^* orbital participates to some extent in the LUMO for conjugated linear polysilylenes¹³ as well as in the SOMO in cyclosilane anion radicals.¹⁴ A comparison of the two spectra also reveals enhancement of the line at 1200 cm^{-1} in the spectrum of the polymer. The rationale for this fact is that this line corresponds to a symmetrical vibration with a complex eigenvector, where not only the deformation of the CH_2 group adjacent to the Si atom, but also the $\nu(\text{Si-C})$ stretching coordinate take part (according to normal coordinate analysis¹⁵). An increase in the intensity of the antisymmetrical $\nu^{\text{as}}(\text{Si-Si})$ vibration—the line at 474 cm^{-1} —is also significant and meaningful.

The results obtained prompt further investigations, whose goal is to elucidate which of the factors mentioned above— δ_i and/or η_i —are responsible for the formation of the intensity of the Raman lines in question. For this purpose it is necessary to study the dependence of the Raman spectra on the wavelength of the exciting light.

It is well-known that elongation of the π - π conjugated chain in a polyene molecule leads to a bathochromic shift of the frequency of the first electronic transition. If the chain is long enough, the first electronic absorption band of these molecules occurs in the near UV or visible spectral region. The Raman spectra of such molecules, provided they are excited in the usual way by visible light, become pre-resonant, exhibiting some peculiar features.¹⁶ In particular, the relative intensity of selected lines appears to be dependent on the wavelength used to excite the Raman scattering, increasing on approaching resonance.

The electronic absorption band of σ - σ conjugated linear poly[dialkylsilylene]s is situated in the near UV region.⁶ The dependence of the Raman spectrum of the polymer $[\text{Hex}_2\text{Si}]_n$ in its all-*trans* conformation, which exhibits a UV band at 370 nm, on the exciting wavelength was demonstrated by Miller, Rabolt *et al.*¹⁷ An analogous dependence was mentioned for $[\text{Me}_2\text{Si}]_n$ ¹⁸ and $[\text{Et}_2\text{Si}]_n$.¹⁹ We have obtained the Raman spectra of $[\text{Pr}_2\text{Si}]_n$ and $[\text{Pr}_2\text{Si}]_5$, using different excitation, from red to indigo, in the visible region. The results for the polymer $[\text{Pr}_2\text{Si}]_n$, which absorbs in the UV at 350 nm, are presented in Fig. 2. To exclude the intensity increase due to the ω^4 law, the spectra were normalized so as to equalize the intensities of the $\delta(\text{C-H})$ lines in the region 1400–1500 cm^{-1} , belonging to the vibrations of CH_2 and CH_3 groups remote from the conjugated backbone. The dependence of the Raman spectra studied on the wavelength of the exciting laser line is apparent. Even with the red excitation a pre-resonance condition still exists, the relative intensity of $\nu(\text{Si-Si})$ and $\nu(\text{Si-C})$ lines being much higher in the spectrum of the polymer than that in the spectrum of the $[\text{Pr}_2\text{Si}]_5$ ring. It is notable that the lines whose intensity is most enhanced on

[†] Similar results were obtained for the analogous diethyl compounds. $[\text{Et}_2\text{Si}]_n$ polymer, with all-*trans* backbone conformation, exhibits resonance enhancement of $\nu\text{Si-C}$ and $\nu\text{-Si-Si}$, whereas the ring compound $[\text{Et}_2\text{Si}]_5$ does not.

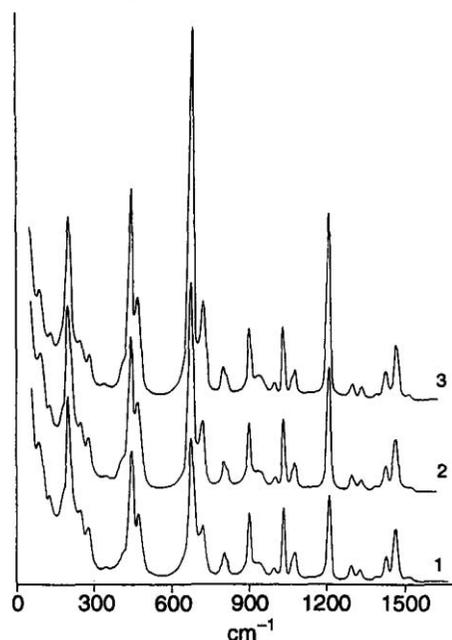


Fig. 2 Exciting wavelength dependence of the Raman spectrum of $[\text{Pr}_2\text{Si}]_n$ (1) 6328 Å (2) 5145 Å (3) 4579 Å.

approaching resonance are exactly the same ones which are affected by conjugation. Again, a spectacular increase in the relative intensity is shown by the line of $\nu^{\text{S}}(\text{Si-C})$ (Fig. 2), pointing to the important role of the Si-C σ^* orbitals in the excited electronic state, 'actual' for Raman scattering.

The Raman spectrum of the small ring $[\text{Pr}_2\text{Si}]_5$, which has its UV absorption band at 260 nm, exhibits no exciting wavelength dependence.

Thus, the data reported here show that σ - σ conjugation in polysilylenes manifests itself in the Raman spectra qualitatively in a similar way to π - π conjugation in polyenes, but exhibits some peculiarities. Quantitative and theoretical investigations of this problem, using the latest theoretical advances in the field of pre-resonance and resonance Raman scattering,^{5,20} are in progress.

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