

Excitation dependence of Raman spectra of various polydialkylsilane conformations and σ – σ conjugation

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Abstract

Excitation dependence of the Raman spectra in a wide region (from blue to infrared) was investigated for hmw polysilanes [ⁿHex₂Si]_n and [ⁿPent₂Si]_n at various temperatures. The results obtained along with analogous data for other polydialkylsilanes lead to the conclusion that among all modifications formed by these polymers, there is only one that exhibits pre-resonance Raman scattering, that is, intensity enhancement and its excitation dependence. This is the crystalline modification with the σ – σ conjugated all-*A* (*anti*) conformation of the silicon backbone. The Raman spectrum of this modification is enhanced by pre-resonance even when $(\nu_e - \nu)$, the difference between the frequency of the lowest energy σ – σ^* electronic transition ν_e and that of irradiating light ν is as much as $\sim 17\,300\text{ cm}^{-1}$, whereas Raman spectra of less-ordered modifications do not exhibit such enhancement even at much smaller $(\nu_e - \nu)$ values, e.g. $\sim 9400\text{ cm}^{-1}$. These facts are discussed in terms of Shorygin's semi-classical treatment of Raman intensity problem. The Raman patterns observed below 800 cm^{-1} allow clear distinction between polysilane modifications with all-*A*, helical (all-*D*) and *TGTG'* (*AD*₊*AD*_–) main chain conformations, whereas helical (all-*D*) and disordered conformations are hardly distinguishable.

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1. Introduction

Raman spectroscopy is well known as an effective tool in investigation of the structure of oligodialkylsilanes, linear [1–4] and cyclic [5,6], as well as in elucidation of structure and conformation of the silicon chain and side groups in polydialkylsilanes [7–31]. Owing to the higher polarizability of Si atoms compared with C and H atoms, the normal modes involving Si atom displacements can be easily identified by their increased Raman intensity.

Among the possible silicon chain conformations of polysilanes (see reviews [32]), one is distinguished by intensity enhancement of Raman lines and its dependence on the frequency of the irradiating light. This was

first demonstrated by Rabolt, Miller et al. [9–11] in the room-temperature form of hmw [ⁿHex₂Si]_n. This polymer form was investigated by a variety of physical methods (the results were summarized in [13,16]), and was assigned as a crystalline modification possessing a planar zigzag all-*trans* (*anti*) conformation of the backbone and ordered side groups. In the UV spectrum it was characterized by an absorption band at $\sim 375\text{ nm}$. The Raman spectrum of this modification exhibited intensity enhancement of the Raman lines corresponding to the stretching vibrations of the Si–Si and Si–C bonds (ν Si–Si and ν Si–C). The most enhanced line was a narrow one at $\sim 690\text{ cm}^{-1}$ corresponding to the ν^s Si–C [10,11]. Later the presence of this intense Raman line was used as diagnostic for the all-*anti* conformation of the backbone in polysilanes with *n*-alkyl side chains longer than Pr [11,18,23,24,26,28,29].

Until recently, it was supposed that the dihedral angles in the fragment SiSiSiSi of a linear homoatomic

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chain $[\text{Si}-\text{Si}]_n$ could have values $\omega = 180^\circ$ (*anti* units) or 60° (*gauche*), as for *n*-alkanes. However, in recent reviews [32a,32b] and a paper [33], on the basis of the results of quantum-chemistry calculations for corresponding oligomers and some experimental data, it has been stated that for polydialkylsilanes the following values of ω may also be realized: $\pm \sim 165^\circ$ (*transoid*, *T*), $\pm \sim 154^\circ$ (*deviant*, *D*), $\pm \sim 90^\circ$ (*ortho*, *O*), as well as 180° (*anti*, *A*) and $\pm \sim 60^\circ$ (*gauche*, *G*). Correspondingly, new designations are recommended: the 7/3 helical conformation all-*D*, etc. (see [33]).

The great Raman intensity increase in the all-*anti* conformation of $[\text{Hex}_2\text{Si}]_n$ and polysilanes with longer side chains was attributed [10,11,17] to a pre-resonance scattering process, arising from the proximity of UV absorption band at ~ 375 nm to the exciting laser lines used, those in the blue–green region. On heating $[\text{Hex}_2\text{Si}]_n$ above its phase transition temperature, $\sim 45^\circ\text{C}$, the UV band at ~ 375 nm disappeared and only the band at ~ 320 nm persisted, corresponding to a hexagonal columnar mesophase (*hcm*). In this form, intermolecular order, but now only two-dimensional, is preserved while both the backbone and the side chains are disordered. According to [10,11], this was accompanied by a dramatic disappearance of all the sharp Raman lines assigned to the silicon vibrations; the Raman spectrum exhibited only very weak broad features. The same result was observed when high hydrostatic pressure was applied to this polymer [17]. This phenomenon was thought [10,11,17] to be due to the shift of the UV absorption from ~ 375 to lower value, ~ 320 nm, away from any resonance interaction with the laser excitation. In other words, the authors [10,11,17] supposed that pre-resonance conditions for their blue-shifted band no longer existed. To our knowledge, this explanation was never questioned in later Raman studies of polydialkylsilanes.

Later other conformations of the polysilane main chain were found to exist, such as 7/3 helix (all-*D*) [12,18,23,34] and the so-called *TGTG'* (*AGAG'*) [13,18,22,29,35] (now thought to have a more open conformation such as *AD*₊*AD*_− [32a]), whose Raman spectra did not show the dramatic intensity enhancement observed for the all-*anti* form. At the same time, the Raman spectra of the polymers $[\text{R}_2\text{Si}]_n$, *R* = Me, Et, ⁿPr [15,19–21,25], as well as those of pressurized $[\text{Bu}_2\text{Si}]_n$ and $[\text{Pent}_2\text{Si}]_n$ [18], whose all-*anti* conformations were believed to be well documented at that time, were all found to exhibit pre-resonance enhancement, yet their UV absorption λ_{max} values were significantly lower than 375 nm. These facts suggest that the correlation between specific silicon chain conformations and the UV band positions may not be straightforward.

In the classical papers of Shorygin, who first discovered resonance Raman effect [36] and described in detail its applications to chemical problems [37], it was

shown that pre-resonance conditions come into play when the difference between the position of the lowest-energy electronic transition ν_e and the exciting laser line ν , that is $(\nu_e - \nu)$, reaches $\sim 40\,000\text{ cm}^{-1}$, and obviously become more effective with lesser values [37]. At the same time, for the helical (all-*D*) and *hcm* polysilane modifications with their ~ 320 nm ($31\,250\text{ cm}^{-1}$) UV band, if the Raman spectrum is excited by the green 514.5 nm laser line ($19\,440\text{ cm}^{-1}$), $(\nu_e - \nu) \approx 11\,800\text{ cm}^{-1}$, that is, well within the pre-resonance region, but no pre-resonance enhancement is observed.

These facts prompted us to investigate in detail the excitation dependence of the Raman spectra of various polysilane modifications, for two of the most thoroughly studied polymers, $[\text{Hex}_2\text{Si}]_n$ and $[\text{Pent}_2\text{Si}]_n$, in order to gain deeper insight into physical grounds of the pre-resonance phenomenon. Another aim of this study is to find out if it is possible to characterize each conformation of the silicon chain formed by various polysilanes by its Raman pattern.

2. Results and discussion

2.1. $[\text{Hex}_2\text{Si}]_n$

This polymer was shown by Lovinger et al. [38] to exist at room temperature as a mixture of a crystalline phase and *hcm*, whose relative proportion strongly depends on preparative conditions. At room temperature, our sample of $[\text{Hex}_2\text{Si}]_n$ exhibited two UV bands at 318 and 372 nm (Fig. 1), corresponding to a coexistence of the *hcm* and all-*A* modifications. Assuming that the intensity of a given UV band is not temperature-dependent (which is, indeed, an approximation), we were able to roughly estimate the amount of *hcm* in our room-temperature sample (as a ratio of integrated intensities of the UV band at 320 nm at room

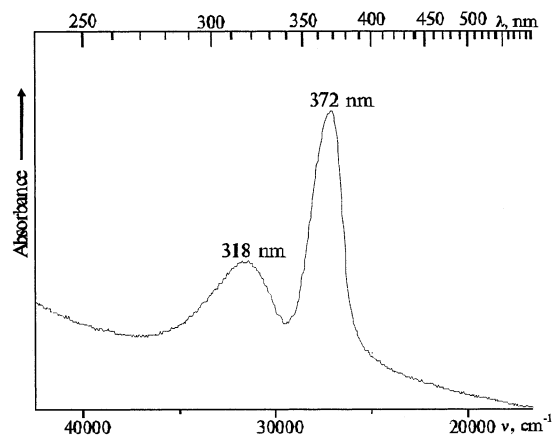


Fig. 1. Room-temperature UV spectrum of the $[\text{Hex}_2\text{Si}]_n$ sample studied, indicating the presence of two modifications in approximate ratio 1:3 (see text).

temperature and above T_c) as $\sim 25\%$. For this sample, in which the all-*A* modification predominates, we have measured the excitation dependence of the Raman spectrum in an extended (from blue to infrared) region (only blue and green lines were used in an analogous previous study [10]). The results are presented in Fig. 2a, b. Relative positions of the [n Hex₂Si]_n UV absorption bands and of the laser lines used for excitation of Raman spectra are depicted in Fig. 3.

In the simplest version of the Shorygin's semi-classical approximation to Raman intensity problem [36,37], each Cartesian component of the derivative of polarizability α with respect to the given normal vibrational coordinate Q_i , $(\partial\alpha/\partial Q_i)_0$, which determines the Raman intensity of the *i*-th normal mode, is given by the Eq. (1).

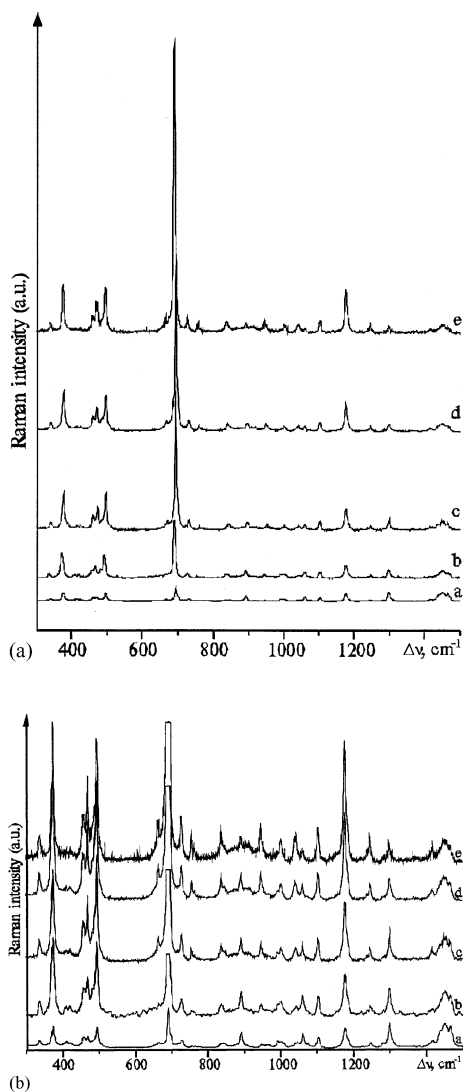


Fig. 2. (a, b) (see text). Excitation dependence of the Raman spectrum of the same [n Hex₂Si]_n sample. Exciting laser lines are 1064 nm (a), 632.8 nm (b), 514.5 nm (c), 488.0 nm (d), 457.9 nm (e).

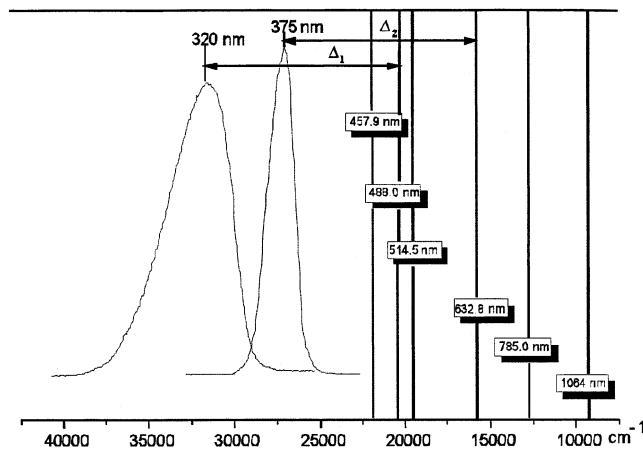


Fig. 3. Relative positions of the [n Hex₂Si]_n UV absorption bands 375 and 320 nm and of the laser lines used for excitation of Raman spectra. Note that the $(\nu_e - \nu)$ differences Δ_1 (~ 10800 cm⁻¹, the distance between 320 nm band and the blue line) and Δ_2 (~ 10900 cm⁻¹, the distance between 375 nm band and the red line) are very close (see text).

The summation is over all excited electronic states *e*:

$$\left(\frac{\partial\alpha_\sigma}{\partial Q_i}\right)_0 = \text{const} \sum_e \frac{\nu_e}{\nu_e^2 - \nu^2} \frac{\partial}{\partial Q_i} (M_\sigma)_{0e}^2 - \frac{\nu_e^2 + \nu^2}{(\nu_e^2 - \nu^2)^2} \times (M_\sigma)_{0e}^2 \frac{\partial\nu_e}{\partial Q_i} \quad (1)$$

where ν_e is a frequency of electronic transition $0 \rightarrow e$, ν is the frequency of the exciting line (usually in the visible region), $(M_\sigma)_{0e}$ is a matrix element of the dipole moment of electronic transition $0 \rightarrow e$.

The first term of Eq. (1) reflects the dependence of electronic transition dipole on vibrational coordinate. However, a more common mechanism of the intensity enhancement encountered in practice was shown to lie in the second term of Eq. (1), in which the resonance denominator is squared. In spite of the fact that in Eq. (1), there is a sum over all the excited levels, for each normal mode there exists an excited level, effective (or "actual", according to Shorygin's term) for the Raman intensity of this particular normal mode. When the exciting line frequency ν approaches the effective ν_e , pre-resonance Raman intensity enhancement should take place, but only for those normal modes which correspond to the stretching vibrations of the bonds localized in that part of the molecule which involves the chromophore bringing about the given ν_e transition. It is well-established [32] that the lowest-energy band in the electronic absorption spectra of polydialkylsilanes corresponds to the σ - σ^* transition localized in the conjugated silicon chain. Thus, on approaching resonance, we should observe an intensity increase for the lines corresponding mainly to the ν Si-Si stretches and to other modes involving silicon atom displacements. At

the same time, the Raman intensity of the modes, not encompassing the silicon chain, but involving only internal vibrations of alkyl groups, should not react to the change in the exciting lines that we used (in visible and infrared region). For intensity of the latter modes, the lowest energy electronic transition localized in the silicon chain is not effective, but rather the electronic transitions situated in the far vacuum UV region (100–150 nm) [37,39] and involving excitations in C–C and C–H bonds. Hence, in order to eliminate the effect of the ω^4 scattering law, we can normalize all the spectra in Fig. 2 so as to equalize the intensities of the bands near 1460 cm^{-1} , corresponding to the deformations of remote CH_2 groups. On examining Fig. 2, it is evident that all the spectra exhibit pre-resonance enhancement of some lines corresponding to $\nu\text{Si-Si}$ and $\nu\text{Si-C}$, including the spectra excited by a red line at 632.8 nm ($\nu_e - \nu \approx 10900\text{ cm}^{-1}$) and even by an infrared line ($\nu_e - \nu \approx 17300\text{ cm}^{-1}$). The latter is demonstrated in Fig. 4 and will be discussed below. Pre-resonant character of all the spectra is not a surprise, because all exciting lines are within Shorygin's pre-resonance region relative to the $\sim 375\text{ nm}$ band.

As the intensity of the line at 690 cm^{-1} exceeds that of other lines many times, Fig. 2 is presented in two versions: a and b. Fig. 2a allows one to follow intensity enhancement of the line at 690 cm^{-1} , while Fig. 2b in which this line is given off-scale presents comparison of other spectral features. Excitation dependence of the intensity ratio of the lines at 690 and 1460 cm^{-1} (I_{690}/I_{1460}) is plotted in Fig. 5. Examining the results presented in Figs. 2 and 5, one should have in mind that our room-temperature sample of $[\text{Hex}_2\text{Si}]_n$ initially contained only ca. 75 % of the all-*A* modification,

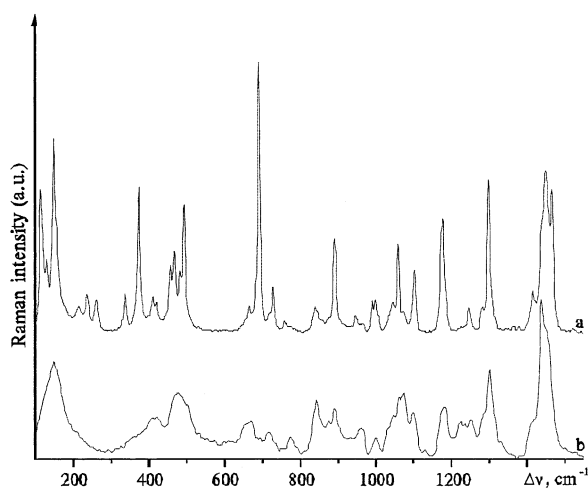


Fig. 4. Comparison of the Raman spectra of the two forms of $[\text{Hex}_2\text{Si}]_n$, both spectra excited by the infrared line 1064 nm . (a) Room-temperature form, containing $\sim 75\%$ of the crystalline phase with all-*A* backbone conformation and ordered alkyl side chains; (b) hexagonal columnar mesophase with disordered backbone and disordered side chains ($60\text{ }^\circ\text{C}$).

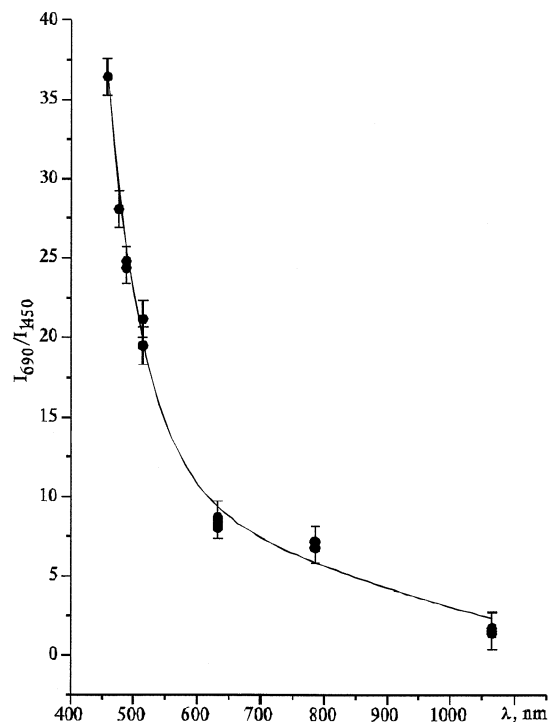


Fig. 5. Excitation dependence of the intensity ratio of the lines at 690 cm^{-1} ($\nu\text{Si-C}$) and 1460 cm^{-1} (δCH_2) in the room-temperature Raman spectrum of $[\text{Hex}_2\text{Si}]_n$.

thus, real intensity enhancement for a pure all-*A* phase would be greater.

The Fig. 2 demonstrate that the line at 1175 cm^{-1} is also excitation-dependent. Previous normal coordinate analyses [40,41] have shown that this line corresponds to a symmetric mode 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.

As was said above, on heating the polymer above its phase transition temperature $\sim 45\text{ }^\circ\text{C}$, only the band at $\sim 320\text{ nm}$ corresponding to *hcm* with disordered silicon backbone persists in the UV spectrum. However, this is not accompanied by a complete disappearance of the Raman spectrum, as was reported in [9–11] (see Fig. 4 in Ref. [11]). The process of this phase transition reflected by our variable-temperature Raman spectrum (from 38 to $45\text{ }^\circ\text{C}$) is presented in Fig. 6. Indeed, instead of sharp lines in the region of the $[\text{SiC}_2-\text{SiC}_2]_n$ skeleton vibrations, above T_c we observe only very broad weak features, but no substantial changes are seen in the region of internal vibrations of hexyl groups, $800\text{--}1500\text{ cm}^{-1}$. We suppose that the disappearance of the Raman spectrum observed in [9–11] was due to a change in optical properties of the polymer on the phase transition leading to defocusing of the scattered light (this is clearly seen on the screen of the microscope of the Raman spectrometer).

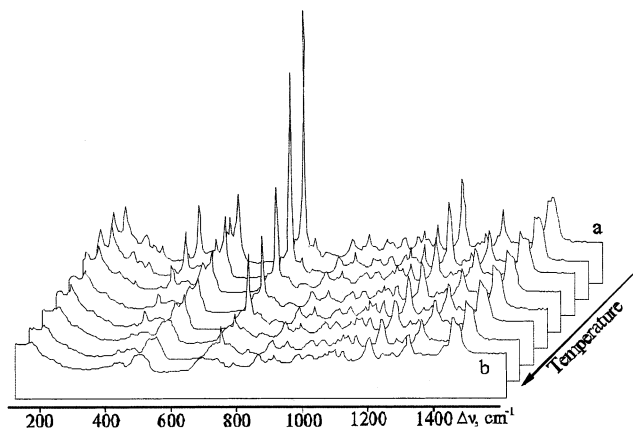


Fig. 6. Temperature evolution of $[{}^n\text{Hex}_2\text{Si}]_n$ Raman spectrum in the region 38–45 °C, reflecting the phase transition. 514.5 nm excitation, (a) 38 °C; (b) 45 °C.

The spectrum of the *hcm* exhibits neither pre-resonance enhancement nor excitation dependence, being identical when excited by the infrared and by the blue 457.9 nm lines (Fig. 7).

Comparison of the Raman spectra of the all-*A* modification and *hcm*, both being excited in the infrared region (Fig. 4), clearly demonstrates that pre-resonance conditions for the all-*A* modification still exist even when $(\nu_e - \nu) \approx 17\,300\text{ cm}^{-1}$, because the sharp band at 690 cm^{-1} is still present in this spectrum and its intensity surpasses that of the feature at 1460 cm^{-1} . An inverse pattern is observed for the *hcm*. Fig. 4 also points to a spectacular side chain disorder in the *hcm*.

From the above results it is evident that Raman intensity decrease observed on going from the crystalline all-*A* modification to *hcm* is *not* due to the shift of the UV absorption from ~ 375 to ~ 320 nm.

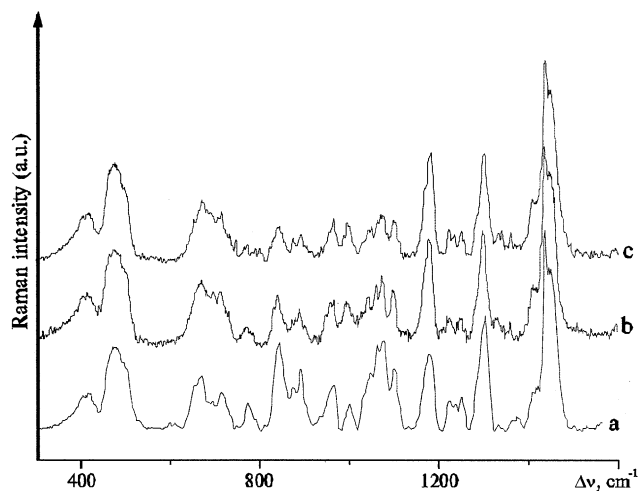


Fig. 7. Raman spectra of the high-temperature *hcm* form of $[{}^n\text{Hex}_2\text{Si}]_n$, at ~ 70 °C, excited by laser lines at 1064 nm (a), 514.5 nm (b) and 457.9 nm (c).

2.2. $[{}^n\text{Pent}_2\text{Si}]_n$

As reported previously [12,23,35], the phase behavior of $[{}^n\text{Pent}_2\text{Si}]_n$ strongly depends on its molecular weight. Unlike $[{}^n\text{Hex}_2\text{Si}]_n$, at room temperature the hmw $[{}^n\text{Pent}_2\text{Si}]_n$ exists as a hexagonal mesophase with macromolecules having 7/3 helical (all-*D*) conformation of the silicon chain and disordered alkyl groups. On heating to 70 °C, this polymer was shown to undergo a solid-state transition but with a very small thermal effect, 2.6 cal g^{-1} [23] (compare analogous effect of 20.0 cal g^{-1} for the phase transition of $[{}^n\text{Hex}_2\text{Si}]_n$ at ~ 45 °C). Such a minor thermal effect suggests a small degree of disordering. Indeed, according to [23,35], upon this transition of $[{}^n\text{Pent}_2\text{Si}]_n$ no change in the intermolecular packing occurs, but only disordering of the main chain, while the alkyl groups remain disordered. However, this structural transition can be unambiguously determined from the UV spectrum (Fig. 8), because the bands corresponding to the helical (all-*D*) form and to *hcm*, both having λ_{max} values near 320 nm, distinctly differ in their contour and half-width (the latter values are 2000 and 3900 cm^{-1} , respectively), the band corresponding to the all-*D* conformation being symmetric and narrower. Above 70 °C, $[{}^n\text{Pent}_2\text{Si}]_n$ forms the same *hcm* modification as $[{}^n\text{Hex}_2\text{Si}]_n$ above 45 °C.

As is seen from Fig. 9, the room temperature Raman spectrum of helical $[{}^n\text{Pent}_2\text{Si}]_n$ is not enhanced by pre-resonance, its most intense feature being that at ca. 1450 cm^{-1} , and exhibits no excitation dependence of the skeletal vibrations, in spite of the fact that its spectrum was excited by a blue line at 476.5 nm, $(\nu_e - \nu) \approx 9400\text{ cm}^{-1}$ (see Fig. 3). It was of great interest to thoroughly investigate the $[{}^n\text{Pent}_2\text{Si}]_n$ structural transition by the Raman method. Detailed comparison of the Raman spectra below and above 70 °C showed that only minor changes take place in the structure of complex features

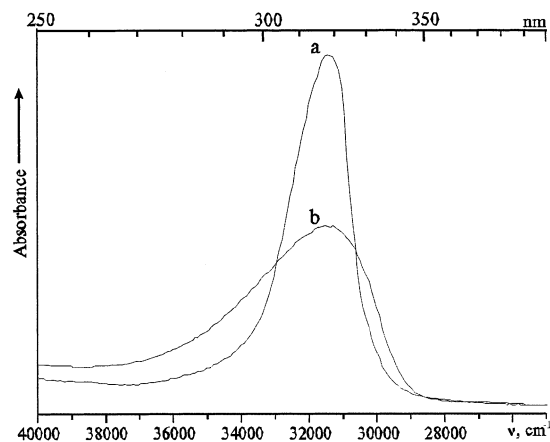


Fig. 8. UV spectra of the hmw $[{}^n\text{Pent}_2\text{Si}]_n$ sample below the structural transition from the all-*D* to a disordered conformation: (a) 24 °C and above (b) 70 °C.

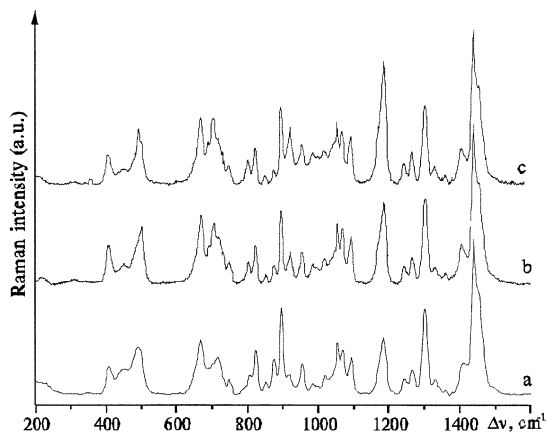


Fig. 9. Raman spectrum of the sample of hmw $[{}^n\text{Pent}_2\text{Si}]_n$ in all-*D* conformation, excited at room temperature by different laser lines. (a) 1064 nm; (b) 514.5 nm; (c) 476.5 nm. Differing band contours in the spectrum *a* compared with *b*, *c* are due to lower resolution of the Fourier–Raman spectrometer used for obtaining *a*.

in the regions $400\text{--}500\text{ cm}^{-1}$ ($\nu\text{Si-Si}$) and $600\text{--}750\text{ cm}^{-1}$ ($\nu\text{Si-C}$) (Fig. 10), the peaks for the all-*D* form being narrower.

Phase behavior of lmw $[{}^n\text{Pent}_2\text{Si}]_n$ was shown to differ from that of hmw sample [23]. Its room-temperature sample contains some modification with the all-*anti* conformation of the backbone along with the all-*D* form. Only the latter modification persists above $35\text{ }^\circ\text{C}$; structural transition from the helical to a disordered form takes place at $56\text{ }^\circ\text{C}$ [23]. Raman spectra of our lmw sample excited by the green line and obtained at three temperatures are presented in Fig. 11. They are in good accord with the data reported in [23]. The spectrum at $23\text{ }^\circ\text{C}$ is evidently enhanced, confirming the presence in the sample of some all-*A* conformation. The spectra at 40 and $72\text{ }^\circ\text{C}$ correspond to the all-*D* and

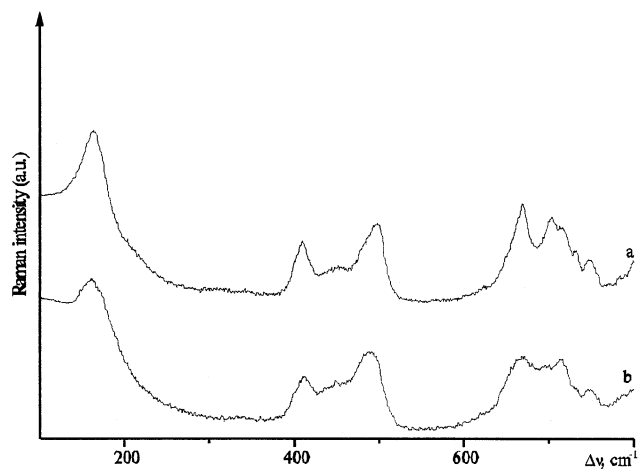


Fig. 10. Comparison of the Raman spectra of hmw $[{}^n\text{Pent}_2\text{Si}]_n$ below and above the structural transition; (a) helical backbone at $20\text{ }^\circ\text{C}$ and (b) disordered backbone at $72\text{ }^\circ\text{C}$. 514.5 nm excitation.

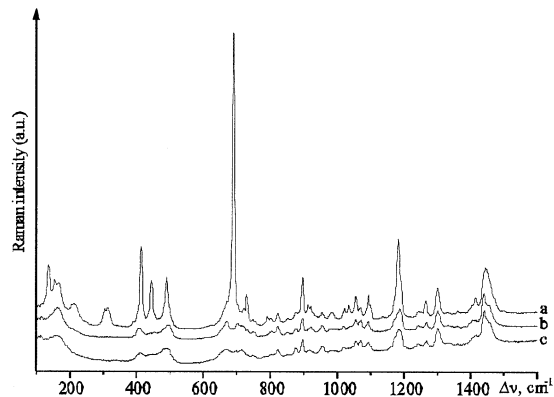


Fig. 11. Raman spectra of lmw sample of $[{}^n\text{Pent}_2\text{Si}]_n$ obtained at different temperatures, 514.5 nm excitation. (a) $23\text{ }^\circ\text{C}$; (b) $40\text{ }^\circ\text{C}$; (c) $72\text{ }^\circ\text{C}$.

disordered forms, respectively, and are identical with corresponding spectra of the hmw sample.

2.3. Generalizations and conclusions

The conclusions that can be drawn from our experiments are as follows:

- 1) Pre-resonance conditions can still be operative when the difference between the positions of the lowest energy electronic absorption band ν_e and the exciting line ν , $(\nu_e - \nu)$, reaches ca. $17\,300\text{ cm}^{-1}$ (the case of the all-*A* form of $[\text{Hex}_2\text{Si}]_n$ with 1064 nm excitation).
- 2) Proximity of ν_e to ν in the resonance denominator of Eq. (1) is necessary but not sufficient for the pre-resonant increase in Raman intensity to occur (the cases of the all-*D* and disordered *hem* forms with excitation in the blue region, when $(\nu_e - \nu) \approx 9400\text{ cm}^{-1}$).

These experimental findings are in good accord with Shorygin's semi-classical treatment of Raman intensity problem, in particular with an important role of the derivative $\partial\nu_e/\partial Q_i$ in the second term of Eq. (1). A necessary condition for pre-resonant Raman scattering is a non-zero value of this derivative, which is related to a molecular geometry distortion in the excited state (the shift of the equilibrium position of an *i*-th vibrational mode upon electron excitation) and thus reflects the specific molecular electronic structure. If this derivative is small, it can cancel out the effect of the resonance denominator. This situation seems to take place for the helical and disordered polysilane forms, whose Raman spectra appeared to be not pre-resonant in spite of proximity of ν_e to ν . Our results suggest a negligible change in the geometry of polysilanes with less-ordered and disordered macromolecules upon electronic excitation.

Thus, the data obtained in this work along with Raman results published for other polydiakylsilanes show that it is only the all-*A* modification that exhibits intensity enhancement and excitation dependence of the Raman spectrum. According to quantum-chemical calculations, planar zig-zag all-*A* conformation favors a maximum degree of σ - σ conjugation in the silicon chain [32].

It is well known that Raman effect is closely related to conjugation. This was first established in the forties by Vol'kenstein [42] and Shorygin [36a] for compounds containing multiple π -bonds. Later this problem was considered by several authors using many examples, and the results were summarized by Shorygin in comprehensive reviews [37]. Conjugation was shown to lead to a small decrease in frequency and a many-fold increase in intensity of the lines, corresponding to the stretching vibrations of the bonds participating in conjugation. It is evident that this is also true of σ - σ conjugation in the polysilane main chain, but only in its all-*A* conformation. To elucidate in detail manifestations of σ - σ conjugation in the Raman effect, the following approach was used [43]. The Raman spectra were recorded and compared for a σ - σ conjugated polymer $[R_2Si]_n$ with its all-*A* backbone conformation [21,25] and of a low-molecular-weight cycle $[R_2Si]_5$ with the same R, both compounds having the same composition (on examples of R = Et, ⁿPr). In the non-planar five-membered cycles, the conditions for conjugation are evidently less favorable. The spectra for R = ⁿPr, excited by a 514.5 nm line, are presented in Fig. 12. As in the case of comparison of all-*A* and *hcm* forms of $[^n\text{Hex}_2\text{Si}]_n$, there is a striking difference between the two spectra in Fig. 12 in the relative intensity of the $\nu\text{Si-Si}$ and $\nu^s\text{Si-C}$ modes, both being greatly enhanced in the spectrum of the polymer. All the above results show that σ - σ conjugation in all-*A* polysilanes affects the Raman intensity qualitatively in the same way as π - π conjugation in polyenes, the effect being strongly dependent on mutual orientation of the conjugating bonds. What is really striking is that the most enhanced are not the $\nu\text{Si-Si}$

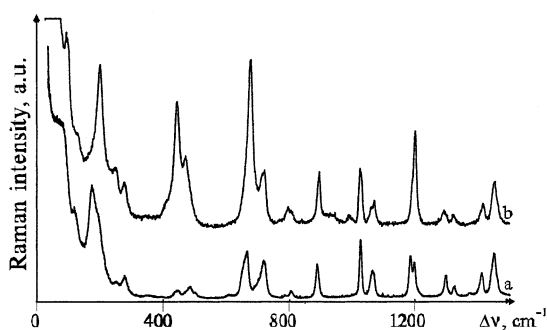


Fig. 12. Comparison of the Raman spectra of solid samples of the cyclic $[^n\text{PrSi}]_5$ (a) and the polymer $[^n\text{PrSi}]_n$ (b). Room temperature, 514.5 nm excitation.

lines, as could be expected for the vibrations of the conjugated silicon chain, but the $\nu^s\text{Si-C}$ line at $670\text{--}690\text{ cm}^{-1}$ which predominates in the spectra. This observation may be explained by two factors. The first one is kinematic coupling of the $\nu\text{Si-Si}$ and $\nu\text{Si-C}$ internal coordinates in the normal mode at $670\text{--}690\text{ cm}^{-1}$. This substantial coupling was demonstrated by the results of normal coordinate calculations reported for $\text{Me}_3\text{Si-SiMe}_3$ [44] and carried out for the repeated unit of the polydimethylsilane $[\text{SiMe}_2\text{-SiMe}_2]_n$ [41]. The second one is electronic (a possible participation of the Si-C σ^* -orbital in the LUMO for conjugated linear polysilanes was proposed by Michl [45]; the ability of the Si-C bond to participate in conjugation was demonstrated in [31] on examples of allylic and benzylic silicon compounds). The role of each of these factors will be the subject for further studies. Anyway, an emergence of the narrow line at $\sim 690\text{ cm}^{-1}$ in the Raman spectrum of a polydiakylsilane in the process of its phase transition serves as an excellent diagnostic for appearance of the all-*A* modification.

If we would like to use the Raman intensity enhancement as a phenomenological criterium of conjugation, as it is commonly done, we would come to an unexpected conclusion that, from the point of view of Raman effect, among the four polysilane backbone conformations studied here only the all-*A* one could be considered as conjugated. This rather strong inference contradicts to the generally accepted point of view [32] and obviously calls for further investigations.

Fig. 13 presents typical Raman patterns observed in the region below 800 cm^{-1} for different conformations of the polysilane backbone. It is seen that all-*A*, all-*D* and AD_+AD_- (proposed [46]) forms are easily distin-

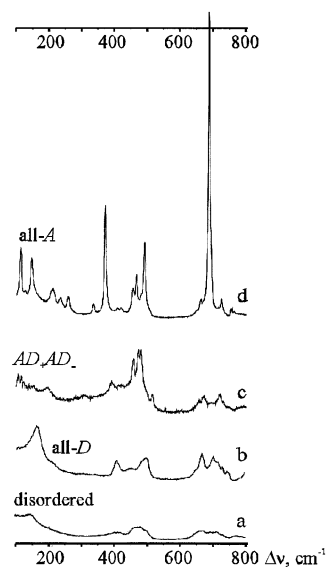


Fig. 13. Typical Raman patterns (in the region below 800 cm^{-1}) of different polydiakylsilane backbone conformations. Ambient temperature, 514.5 nm excitation.

guishable, while it is rather difficult to distinguish between the all-*D* and disordered forms.

As was said above, the Raman intensity enhancement is observed for the room-temperature crystalline modifications not only of [$^n\text{R}_2\text{Si}$] $_n$ with R = Hex, Hept, Oct [9–11], all exhibiting a UV band at ~ 375 nm, but also of [Me_2Si] $_n$ [15,20], [Et_2Si] $_n$ [15,21], [$^n\text{PrSiMe}$] $_n$ [30,31], [$^n\text{Pr}_2\text{Si}$] $_n$ [25], as well as for pressurized or low-temperature modifications of [$^n\text{Bu}_2\text{Si}$] $_n$ and [$^n\text{Pent}_2\text{Si}$] $_n$ [18,23], yet their UV absorption λ_{max} values are significantly lower than 375 nm, being 342, 352, 341, 355, 350, and 362 nm, respectively. Until recently, the all-*A* conformation of the backbone for all these modifications was believed to be well documented. However, in the reviews [32a,32b], the values 340–355 nm are considered as too low for a fully-extended polymer chain and the structural assignment of these modifications as all-*A* is regarded as somewhat doubtful, all-*T* conformations seeming preferable (indeed, Lovinger and coworkers mentioned that small statistical departures from true *trans*-planarity may be present in [Et_2Si] $_n$ and [$^n\text{Pr}_2\text{Si}$] $_n$ [47]). The argument is that twisting of the chain away from the 180° dihedral angle leads to successively higher σ – σ^* energies, shifting the absorption to shorter wavelength.

However, there could be other explanations of the λ_{max} lowering, such as a decrease in effective length of *anti* sequences in smaller-size crystalline lamellas, formed by the macromolecules of the given polymer [16,48,49], or the influence of crystal packing forces [50]. Whatever explanation is correct, from the Raman point of view, all the polymer modifications listed in the above paragraph are alike, in spite of the difference in their λ_{max} , all their Raman spectra exhibit similar intensity enhancement and excitation dependence, pointing to σ – σ conjugation.

3. Experimental

Both polymers were synthesized in a usual way for polysilanes, by Wurtz coupling reaction [32]. The molecular weight and polydispersity for [$^n\text{Hex}_2\text{Si}$] $_n$ were 345 000 and 2.1, respectively. Two samples of [$^n\text{Pent}_2\text{Si}$] $_n$ were studied: a hmw 870 000 and a lmw 37 000.

The same polymer sample was used for registration of Raman and UV spectra in order to rule out uncertainties due to different conditions of sample preparation and make the results of the two methods strictly comparable. Polymer samples were prepared as either thin films cast from solutions in cyclohexane ($c = 0.1$ – 0.5 mol unit l^{-1}) on quartz plates with subsequent evaporation of the solvent or as small amounts of a bulk, as-prepared powder placed between thin quartz

windows and slightly pressed with simultaneous rotation of one window relative to the other.

UV absorption spectra were registered using a computerized Carl Zeiss M-40 spectrophotometer. Raman spectra were obtained using a Jobin–Yvon T64000 laser Raman spectrometer equipped with a CCD detector cooled by liquid nitrogen and a microscope. This high-sensitivity installation allows us to investigate by the Raman method the very same samples as in the UV experiments. For the study of excitation dependence of Raman spectra, a U-1000 and a LabRAM Jobin–Yvon laser Raman spectrometers were also applied. Various lines were used for Raman spectra excitation: those at 457.9, 488.0, and 514.5 nm from Ar⁺ lasers Spectra Physics 2020 and Carl Zeiss ILA 120, that at 632.8 nm from a He–Ne laser GALAMED, and that at 785 nm of a diode laser. To obtain the Raman spectra with excitation by the 1064 nm line, a Fourier–Raman spectrometer Bruker RSF 100 was used. To minimize laser-induced heating and to avoid radiation damage of the specimen, the laser power did not exceed 10 mW.

In variable-temperature experiments an electric heater was used. The temperature was controlled by a Pt resist RTD (100 Ohm), which was inserted directly into the sample under study, and measured by a temperature indicator DP41-U Omega with accuracy ± 2 °C.

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