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Variable-temperature UV and Raman study of complicated thermochromic phase transition of order—disorder type in poly(di-*n*-decylsilane) $[(n\text{-}C_{10}H_{21})_2Si]_n$*

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A complicated thermochromic phase transition (PT) of order—disorder type in poly(di-*n*-decylsilane) has been studied in detail by variable-temperature UV and Raman spectroscopy. Not less than five polymer modifications were shown to participate in this PT. Above the equilibrium PT temperature T_c (~60 °C), the polymer exists as a hexagonal columnar mesophase (HCM) with a disordered silicon backbone and disordered side chains. PT proceeds not abruptly but over a temperature range 60—5 °C and does not reach completion, being stopped by glassification. At room temperature, a coexistence in the polymer of HCM and a few crystalline phases with ordered backbone is observed. The latter are separated in space, what was evidenced by Raman micromapping of a polymer film. The temperature intervals of existence of different ordered phases also do not coincide, this enables one to identify in the UV and Raman spectra the components, corresponding to the modifications possessing *trans* (*anti*) and, supposedly, AD_+AD_- main chain conformations. As the relaxation processes in this comb-like polymer occur slowly, the quantitative ratio of different phases is not a single-valued function of temperature but depends on the thermal prehistory of the sample. Ordering of long side chains on cooling was demonstrated by the Raman method.

Key words: poly(dialkylsilanes), phase transition, thermochromism, ordering, UV and Raman spectroscopy.

Linear poly(dialkylsilanes) of the type $[RR'Si]_n$ attract much attention due to their unique properties (see reviews[2—5]). In spite of the fact that their main chain consists of only silicon atoms linked by ordinary σ-bonds, these polymers exhibit a complex of features typical for π—π-conjugated systems and determined by electron delocalization (*e.g.* conductivity, nonlinear optical properties, *etc.*). It is common practice to call these polymers "σ—σ conjugated" ones. All poly(dialkylsilanes) absorb in the near UV region (300—400 nm), the position of the absorption band being dependent on the length and conformation of the main chain and can vary with temperature (thermochromism).

Until recently, it was supposed that the dihedral angles in the fragment M—M—M—M of a linear homoatomic chain $[M—M]_n$ could have values $\omega = 180°$ (*trans* or *anti* units) or 60° (*gauche*), as for *n*-alkanes. However, in the recent reviews[2a,b] and a paper,[6] on the basis of the results of quantum-chemistry calculations and some experimental data, it is stated that for poly(dialkylsilanes) with their bulky substituents also the following values of ω could be realized: ±165° (*transoid*, *T*), ±154° (*deviant*, *D*), and ±90° (*ortho*, *O*). Correspondingly, new designations are recommended; for instance, the planar zigzag chain conformation with $\omega = 180°$ is named *all-A* (instead of all-*trans*), the 7/3 helical conformation *all-D*, *etc.* (see Ref. 6).

Experimental and theoretical data show that the planar *all-A* structure of the main chain (Fig. 1, *a*) is the most favorable for σ—σ conjugation; this conformation exhibits the most red-shifted UV absorption band. An interesting property of polysilanes is that they undergo phase transitions (PT) of the first order and of order—disorder type, which involve the change in the conformation of the silicon backbone. This leads to a characteristic change in the UV absorption spectrum, where new bands appear, which makes UV spectroscopy a very sensi-

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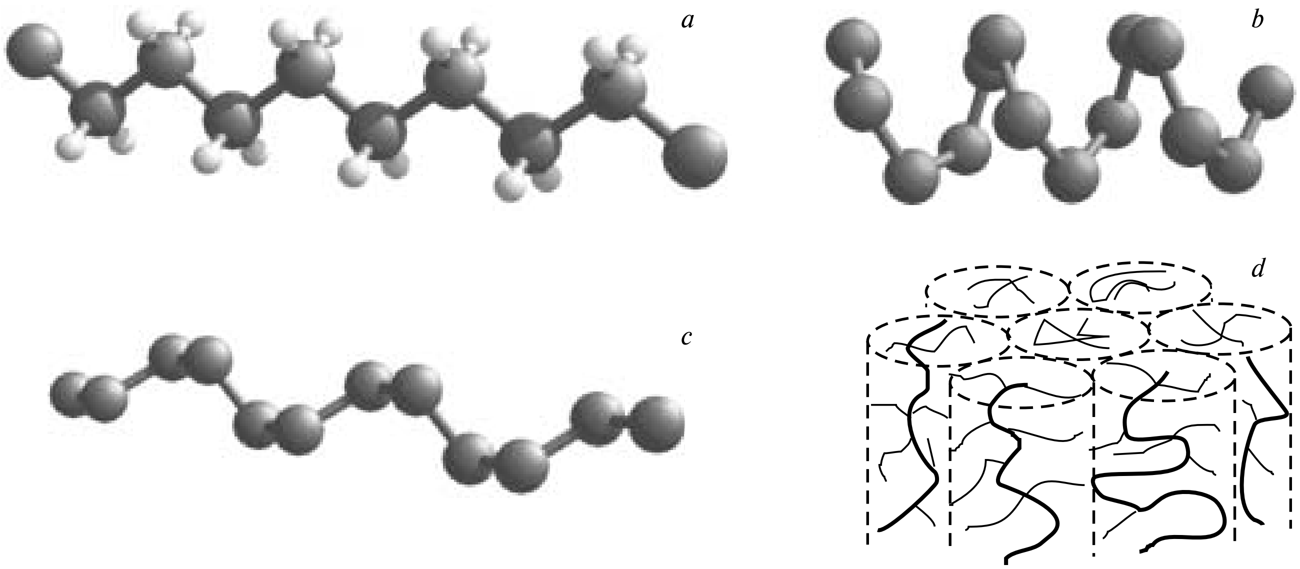

Fig. 1. Possible conformations of the poly(dialkylsilane) main chain: planar *trans* (*all-A*) (*a*), helical (*b*), *TGTG′* (*AGAG′*) (*c*), and hexagonal columnar mesophase with a disordered main chain (*d*).

tive method in PT studies. Raman spectroscopy is informative as well in this instance, for the Raman spectra allow one to elucidate the conformational state of the main chain and its degree of conjugation[7] and also examine conformational transformations in the alkyl substituents.[7b,8]

The nature of PT of the symmetrically substituted polysilanes $[R_2Si]_m$ ($R = n\text{-}C_nH_{2n+1}$) has been studied most extensively. The leading role appeared to be played by the length of the side alkyl chain n, it affects the temperature of the phase transition, the structure of the ordered phases formed and thus the shift of the electronic absorption band. Above T_c, the equilibrium PT temperature,* all these polymers exist as a hexagonal columnar mesophase (HCM) with a disordered skeleton of the macromolecules; however, the latter are as if "inscribed" within virtual hexagonally packed cylinders forming a two-dimensional crystal[10,11] (Fig. 1, *d*). In the UV spectrum, HCM is characterized by a broad absorption band with $\lambda_{max} \approx 320$ nm.

The polysilanes with $n = 1$—3, that is, with short alkyl "tails" [12—20] are highly crystalline at room temperature and exhibit *trans* (*all-A*) or nearly *all-A* conformation of the main chain, to whom the UV band in the region 350 nm corresponds. Phase transformation of these crystalline polymers to HCM takes place at temperatures above 200 °C, if at all.

The polysilanes with $n = 4$ and 5 at room temperature form the modification in which the macromolecular skeleton adopts the 7/3 helical (*all-D)* conformation (Fig. 1, b). The UV band corresponding to the latter conformation lies in the same region as that for HCM, but these two conformations can be distinguished by the band width and contour.[21a,22] Heating of these polymers to 80 °C leads to a PT into HCM.[16,21a] If specific conditions are met (high pressure, preparation of the polymer film from solution at low temperatures, *etc.*), one can obtain these polymers in *trans (all-A)* conformation exhibiting a UV band at 355 nm.[21b,c,23—26]

Phase transitions of polysilanes with $n = 6$—8 are of the same nature as those for $n = 1$—3 but occur at lower temperatures near 50 °C and their *all-A* modifications are characterized by a more red-shifted band in the UV spectrum (365—380 nm).[11,16,24a,25,27—33]

As for polysilanes with longer side chains, there is an X-ray study,[33] which reports that the low-temperature crystalline phase of the polymers with $n = 9$—14 is formed by macromolecules in *TGTG′* conformation (*AGAG′*, according to the new designation[6]) (Fig. 1, *c*) exhibiting a UV band with $\lambda_{max} = 350$ nm. At the same time, in a review[2d] it was mentioned that in poly(di-*n*-decylsilane) (PDDS, $n = 10$) below T_c two crystalline phases coexist, to which the UV bands with λ_{max} at 350 and 378 nm correspond. The intensity ratio of these bands was noted to depend on the polymer molecular weight and on thermal history of the sample. The DSC data for PDDS [34] reveal two endothermal peaks upon heating, those at 35 and 55 °C, but only one exothermal peak upon cooling (at 21 °C). The authors[34] consider these results together with the UV data in terms of existence of the polymer at low

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* In this paper, we mean by the term "equilibrium phase transition temperature" the temperature, at which the rest regions of the more ordered phase disappear in the polymer sample, provided the process is carried on under quasi-equilibrium conditions (see discussion of this point in the monograph[9]).

temperature in *all-A* conformation (λ_{max} =378 nm) and appearance of an intermediate *AGAG´* phase ($\lambda_{max} \approx$ 350 nm) in the process of heating. Investigation of PDDS was continued[35] by DSC and solid-state NMR ^{29}Si and ^{2}H methods. Again, a strong dependence of the results on the thermal prehistory of the sample was demonstrated. The authors consider their NMR data as pointing to existence of this polymer in two crystalline states, one of which corresponds to a "pure" phase with *transoid* backbone conformation; the nature of the second is not determined. Thus, literature data on the nature of the PT of PDDS are not unambiguous.

The aim of this work is a detailed investigation of the nature of thermochromic PT in PDDS using variable-temperature UV and Raman spectroscopy. Analogous studies carried out for other poly(dialkylsilanes), both symmetrically and unsymmetrically substituted, were published by us previously.[7,12,17,20,22,36–39] In order to eliminate the effect of thermal prehistory of the sample on the experimental results and to have a possibility of strict comparison of the data obtained by different methods, the UV and Raman spectra were recorded for one and the same sample, a thin polymer film.[7b,c,38,39] As a result, it has been shown that each of all possible polymer modifications can be related to a definite Raman pattern in the regions of the ν(Si—Si) and ν(Si—C) stretching vibrations and to a definite band in the UV spectrum. In the latter case not only the λ_{max} of the band but also its half-width and contour should be necessarily taken into consideration.[7b,22,36–39] The same approach was applied to PDDS.

Experimental

The polymer $[(n\text{-}C_{10}H_{21})_2Si]_n$ was synthesized in a usual way for polysilanes, by Wurtz coupling reaction,[2] M_w = 412000. For spectral studies, polymer samples were prepared as thin films cast from solutions in hexane (C = 0.1—0.5 mole unit L^{-1}) on quartz plates with subsequent evaporation of the solvent. To obtain uniform polymer films with reproducible properties, a special technique was devised, analogous to that used in fabrication of photo films.

UV absorption spectra were registered using a Carl Zeiss M-40 spectrophotometer. Raman spectra were obtained using a Jobin-Yvon T64000 laser Raman spectrometer equipped with a microscope and a high-sensitivity CCD detector cooled by liquid nitrogen. This installation allows one to investigate by the Raman method the very same thin films as in the UV experiments. The Raman spectra were excited by the 514.5 nm line of an Ar$^+$ laser Spectra Physics 2020. The laser power did not exceed 10 mW in order to avoid substantial heating or destruction of the polymer. Micromapping of the PDDS sample was accomplished using a Raman spectrometer Labram (Dilor-Jobin-Yvon) with a microscope; the spectra were excited by the 632.8 nm line of a He—Ne laser.

A thermostat U7^c was employed for variable temperature measurements. The quartz plate with the polymer film was placed in a massive copper holder of a vacuum cryostat. The temperature was maintained and controlled with an accuracy of ±1 °C using a thermocouple or a Pt resist (100 ohm), which were inserted directly into the film under study. The temperature was changed in a stepwise manner; after each temperature change of several degrees, the sample was allowed to relax at a given temperature until the spectrum stopped altering (not less than 1.5 h), that is, the process was carried out under quasi-equilibrium conditions.

For spectra treatment and curve-fitting analysis of complicated UV absorption contours, a file of appropriate computer programs was applied allowing continuous varying of the parameters (position, half-width, and contour) of individual bands brought in the curve-fitting procedure (ORIGIN 7.0 and SPECTRUM, the latter program was modified by one of the authors).

Results and Discussion

DSC data

Preliminarily, DSC data were collected for the polymer studied (with a heating rate of 8 °C min^{-1}). Further spectral experiments have shown that this rate does not allow the sample to follow the temperature change in equilibrium conditions. Nevertheless, the DSC results obviously point to a complex nature of PT because the DSC curve clearly demonstrates two broad signals in the temperature interval 30—60 °C (Fig. 2) in good accord with the literature data.[34,35]

UV spectra

The film just after preparation and its relaxation at room temperature. The UV spectrum of a freshly cast film of PDDS at 19 °C is given in Fig. 3, curve *1*. According to literature data,[2] a broad band with $\lambda_{max} \approx$ 320 nm (band I) corresponds to HCM. A complex absorption with submaxima at 365 nm (band III) and 385 nm (band IV) is

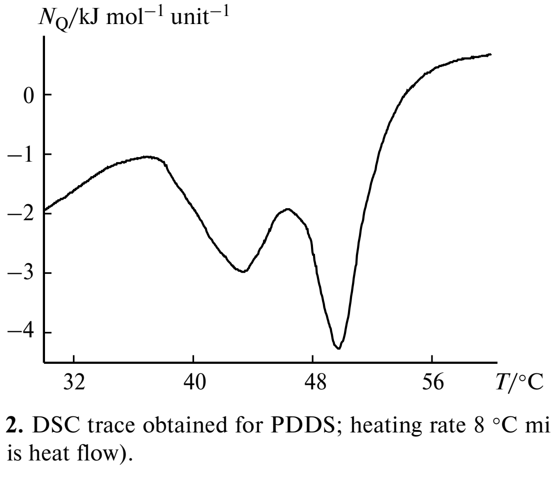

Fig. 2. DSC trace obtained for PDDS; heating rate 8 °C min^{-1} (N_Q is heat flow).

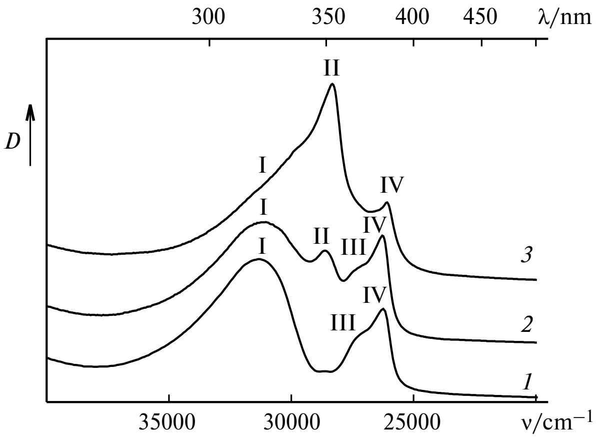

Fig. 3. Room temperature UV spectra of a freshly cast PDDS film (*1*); of the same film after 12 h of isothermal relaxation at ~19 °C (*2*), and after repeated thermal treatment (*3*).

also present in this spectrum. After 12 hours of isothermal relaxation of the film at ~19 °C, the spectrum has changed significantly (see Fig. 3, curve *2*). The relative intensities of bands I and III have decreased, and a band at 350 nm (band III) which was hardly seen in Fig. 3, curve *1* has become distinct. Evidently, the bands in the region 350—385 nm belong to the polymer modifications having a more ordered skeleton of macromolecules. We shall designate the PDDS modifications by the same numbers as the corresponding UV bands. Thus, after long relaxation at ~19 °C, a coexistence of the disordered HCM (I) and three more ordered modifications (II—IV) is observed in the polymer. The bands with $\lambda_{max} \approx 350$ and 378 nm were observed for PDDS previously[2d,34,35] and were assigned to the *TGTG′* (*AGAG′*) and *trans* (*all-A*) conformations of macromolecular backbone in crystalline modifications, respectively. This assignment, as well as that of band III, will be discussed below, after presenting all the results obtained.

First heating to T_c. The temperature evolution of the UV spectrum of the PDDS film, previously held at ~19 °C (its spectrum was given in Fig. 3, curve *2*) is presented in Fig. 4. Heating of the sample leads to an increase in intensity of band I at the expense of the intensities of the "ordered" bands. However, the latter were found to exhibit different temperature behaviors. Band IV disappears first, on heating to ~40 °C. The second to disappear is band III, which persists until ~45 °C. Band II is the last to disappear, at ~60 °C, when the PT reaches completion and only the broad band I is seen in the UV spectrum.

First cooling. After completion of the PT, the same sample was cooled to 47 °C and held at this temperature for 15 hours. However, this does not lead to an expected appearance of the "ordered" bands in the UV spectrum; only band I was observed (Fig. 5, curve *1*). This is obviously due to a strong hysteresis phenomenon, typical for high-molecular-weight comb-like polymers. Only cooling to ~40 °C, with subsequent isothermal relaxation at this temperature for two hours, leads to a simultaneous appearance in the UV spectrum of bands III and IV (see Fig. 5, curve *2*). When the sample was maintained at 40 °C for a further 25 hours, a slow growth of the intensi-

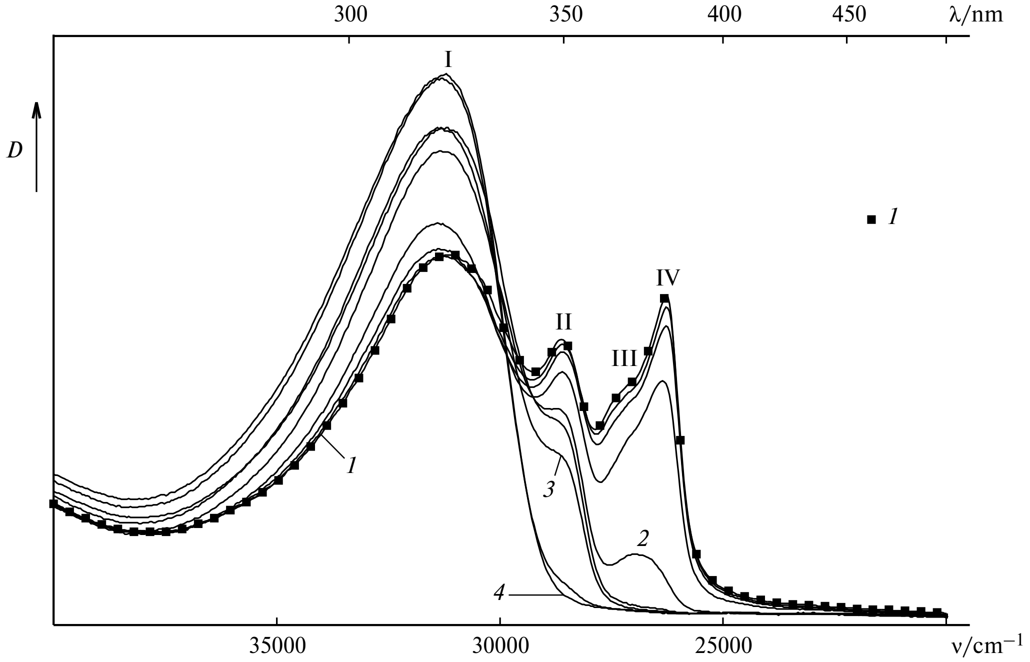

Fig. 4. Temperature evolution of the UV spectrum of a PDDS film in the course of the first heating: initial film (*1*) (19 °C), 40 (*2*), 45 (*3*), and 60 °C (*4*).

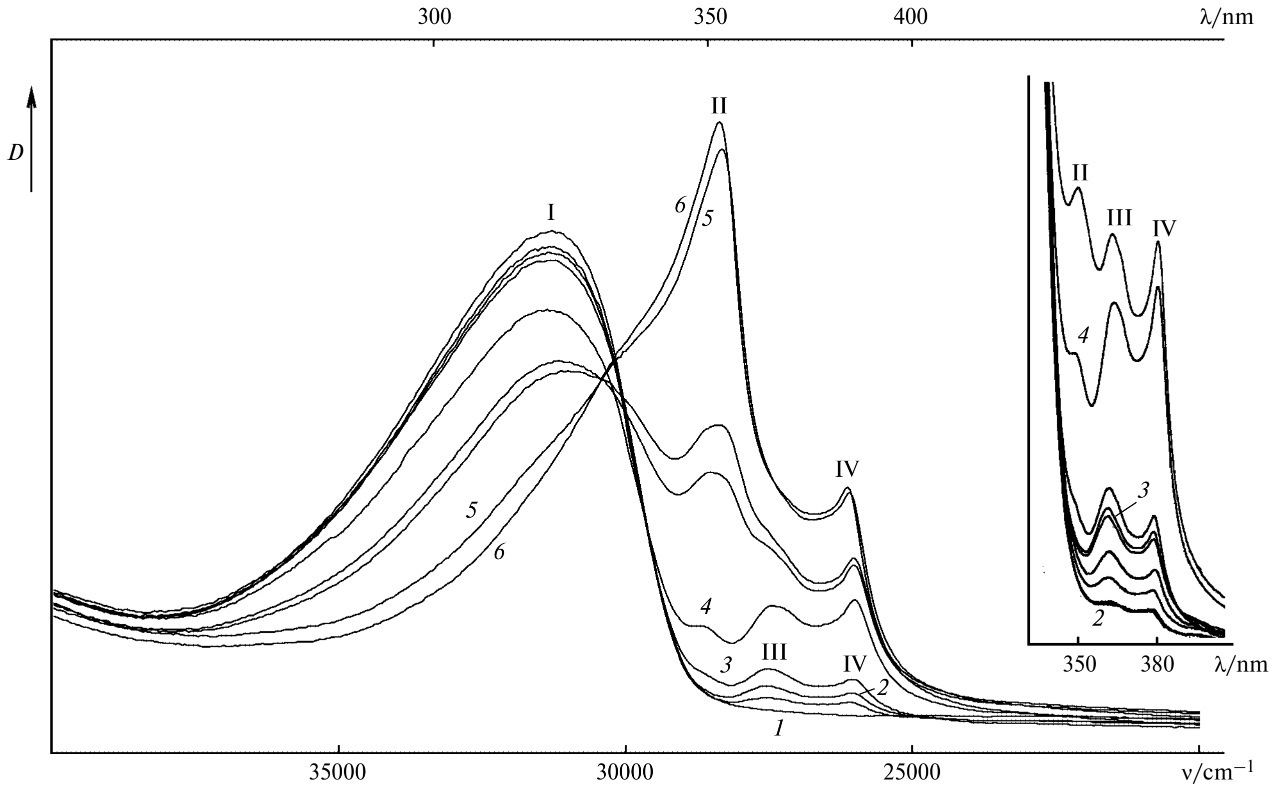

Fig. 5. Temperature evolution of the UV spectrum of the same PDDS film in the course of the first cooling (immediately after the first heating shown in Fig. 4) down to 47 (*1*), 40 (*2*, *3*), 35 (*4*), 19 (*5*), and 5 °C (*6*) (curve *3* was obtained after 25 hours of isothermal relaxation). The inset presents the spectral region λ = 350—400 nm in more details.

ties of bands III and IV was observed (see Fig. 5, curve *3*). Band II appeared in the spectrum only after the temperature lowering to 35 °C followed by isothermal relaxation for 3 hours (see Fig. 5, curve *4*). The inset in Fig. 5 reflects this stage of PT in more detail. Further continuous slow cooling from 35° to 5 °C for 115 hours resulted in a reduction in intensity of band I and an overall increase in intensity of the "ordered" bands (see Fig. 5, curves *5* and *6*). Band II grows the most rapidly, its intense wing begins to superimpose on band III and mask the latter. It is remarkable that the spectral pattern, recorded at 19 °C in this experiment with band II dominating (curve *5* in Fig. 5), differs dramatically from the patterns observed at the same temperature but before thermal treatment of the film. This is spectacularly demonstrated by Fig. 3, where curve *3* corresponds to curve *5* of Fig. 5.

Thus, a cycle of thermal treatment (heating—cooling) leads to the enrichment of the sample with the kinetically hampered modification II.

As is seen from Fig. 5, band I does not disappear completely even at 5 °C. Further cooling alters the UV spectrum negligibly; it seems that at 5 °C polymer glassification takes place which always cancels the processes of such PTs, "freezing out" the necessary molecular mobility.

Second heating. After the first "heating—cooling" cycle, the same film of PDDS was exposed to heating to T_c again, but this time with a different initial ratio between disordered and ordered forms. This process of PT is reflected by the UV spectra given in Figs. 6, *a* and *b*. The intensity of band IV begins to diminish upon heating above 17 °C, and this band disappears completely at 50 °C. The intensity of band II starts to decrease rapidly only above 45 °C and the band disappears completely at ~60 °C.

Further experiments and discussion of the UV spectra. The scenarios of further experiments are, in essence, the same as described in two previous sections, but the processes proceed more "easily." In particular, during the second cooling, bands III and IV became noticeable already at 48 °C while during the first cooling they appeared only at ~40 °C.

Variable-temperature UV study of the given PDDS film was carried out continuously for 385 hours under quasi-equilibrium conditions. The results obtained show that in the temperature interval between $T_c \approx 60$ °C and glassification point $T_g \approx 5$ °C the polymer undergoes a reversible thermochromic PT. This transition is of complex origin and involves HCM and at least three more ordered modifications, whose concentration between T_c and T_g is not a single-valued function of temperature but

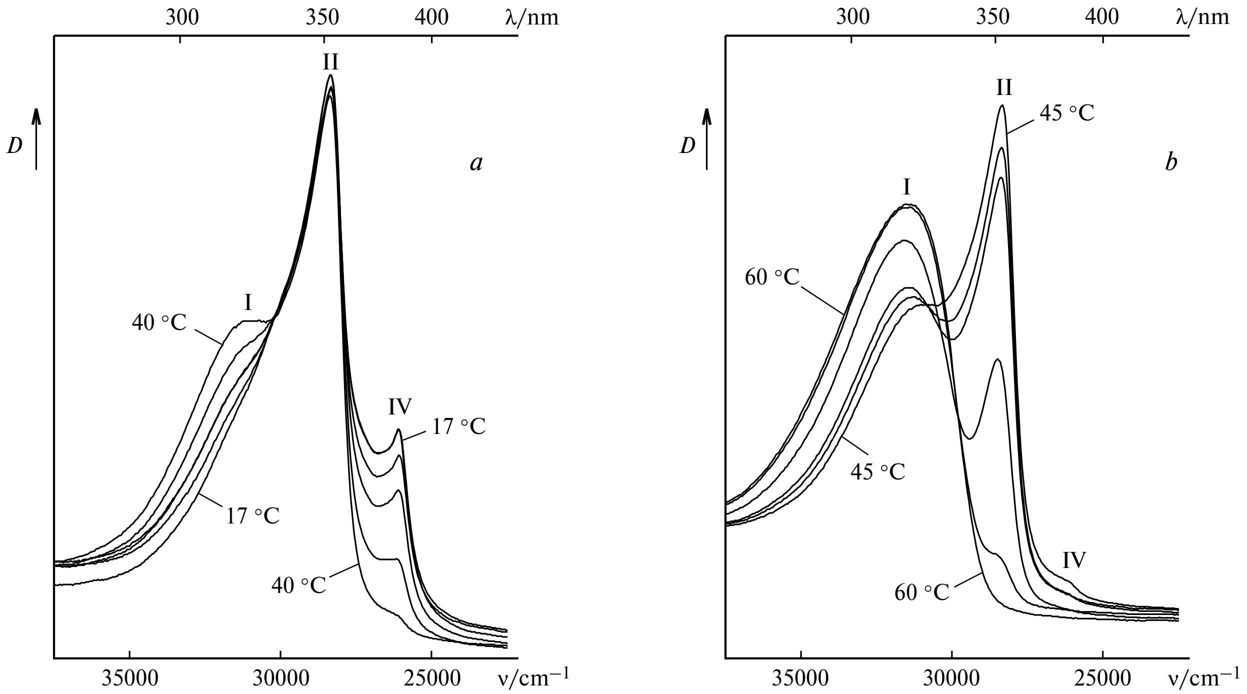

Fig. 6. Temperature evolution of the UV spectrum of the same PDDS film during the second heating in the temperature intervals 17—40 °C (*a*) and 45—60 °C (*b*).

strongly depends on the thermal prehistory of the sample. The latter statement is clearly illustrated not only by Figs. 3—6 but also by Fig. 7 where the temperature evolution of the UV spectra of other samples of PDDS upon their spontaneous cooling from T_c to ~19 °C are shown. Fig. 7, *a* corresponds to a freshly prepared film, heated to T_c, while Fig. 7, *b* to a film heated to T_c repeatedly. These two patterns differ not only in the content of band II, but also in relative intensities of bands III and IV.

Complicated profiles of the UV absorption observed in the course of PT (see Figs. 3—7) result from the superposition of several individual bands. In order to determine parameters of the latter, we had to resort to the procedure of computer curve-fitting analysis of the recorded contours. It is well known that this procedure is, generally speaking, not unambiguous. However, due to systematization and analysis of the UV spectra of many poly(dialkylsilanes) studied we became well aware that each of the modifications formed by polysilane macromolecules is characterized by its own UV absorption band, each with its definite value of λ_{max} and half-width $\Delta\nu_{1/2}$ and in possession of a definite contour. It was also found that these parameters are slightly but regularly temperature-dependent. All said above is also true of PDDS. This can be seen from the data of Table 1, where the average values of λ_{max} and $\Delta\nu_{1/2}$ are given, measured for the UV bands of PDDS and also derived from the computer curve-fitting analysis of complicated absorption contours (an example of the latter is presented in Fig. 8). The more ordered the polymer modification, the more red-shifted and narrow is the corresponding UV band.

Table 1. Position (λ_{max}) and half-width ($\Delta\nu_{1/2}$) of absorption bands observed in the UV spectra of PDDS in the course of the phase transition

Band number	λ_{max}/nm	$\Delta\nu_{1/2}$/cm^{-1}	Main chain conformation
I	320	4000	Disordered in HCM
II	350	1200	AD_+AD_-
III	365	1100	*all-A* or *all-T*
IV	380	900	*all-A*
V*	340	2200	—

Notes. The λ_{max} and $\Delta\nu_{1/2}$ values are slightly but regularly temperature-dependent, that is why in Table 1 their approximate average values are given.

* Band V manifests itself distinctly only after computer curve-fitting analyses of some complicated contours.

In the process of a PT with the participation of several polymer forms, a regular evolution of complicated UV absorption profile is observed, which is due only to a gradual redistribution of these band intensities without significant change in their parameters. Thus, if the parameters of the absorption bands, characteristic of each of the participating modifications, are known, at least in the first approximation, then computer curve-fitting analysis of the complicated contour becomes less arbitrary.

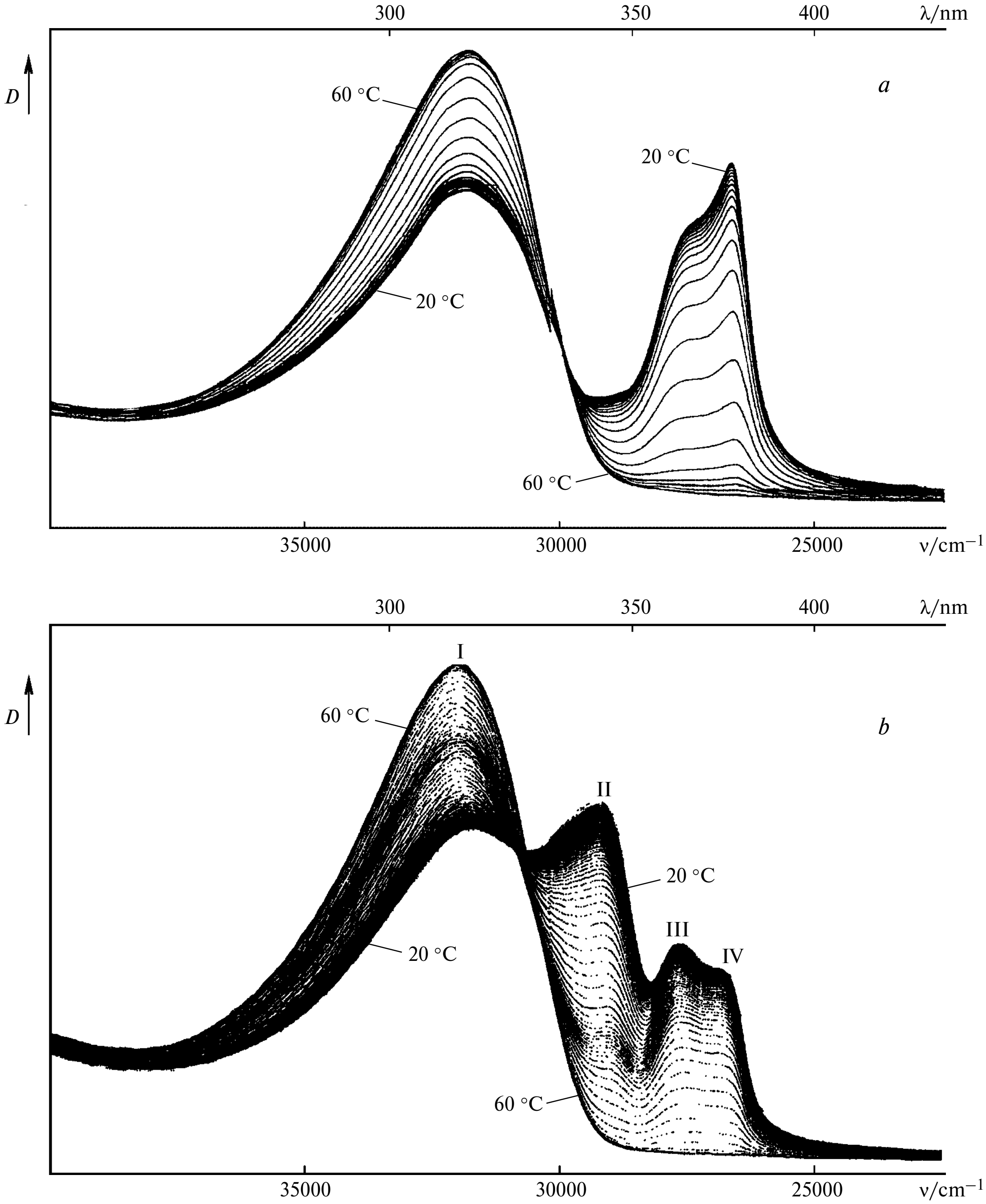

Fig. 7. Temperature evolution of the UV spectra of other PDDS samples heated above T_c on their spontaneous cooling to ~19 °C (see text): a freshly prepared film (*a*) and the film after thermal treatment (*b*). The spectra were recorded continuously during several hours, each scan took 3 min.

Even if the parameters of the band corresponding to a given modification are not known *a priori*, in some cases they are nevertheless determinable, since among the absorption contours observed one can find those whose particular shape obviously dictates the number of individual bands which should be included in the curve-fitting procedure. Sometimes the parameters of these bands can be also evaluated. For instance, the presence of sharp peaks with λ_{max} ≈ 350 and 378 nm, which stand out from the absorption curves (see Figs. 6, *a*, *b*) makes it necessary to introduce into the curve-fitting procedure the corresponding narrow individual bands II and IV. Another example is given in Fig. 3, curve *1*, where the UV absorption curve is an evident superposition of broad asymmetric indi-

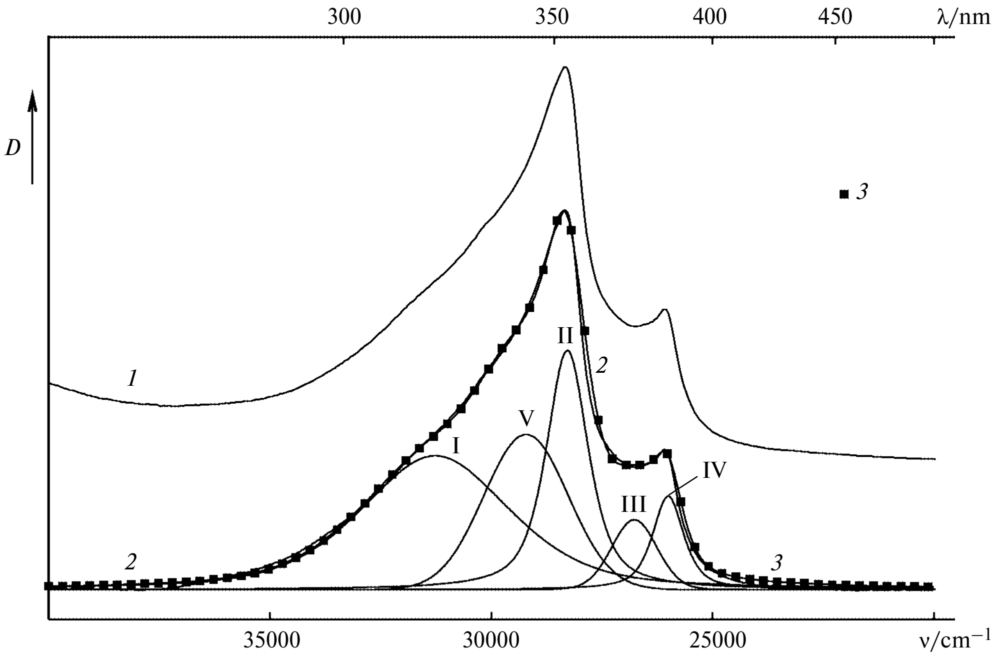

Fig. 8. An example of computer curve-fitting analysis of a complicated PDDS UV absorption with participation of five individual components: experimental curve (*1*), the same curve after base line subtraction (*2*), individual components I—V, and their summary curve (*3*).

vidual band I (whose parameters are known from the spectrum registered at $T > T_c$) and of two narrow overlapping bands III and IV. Thus, experimental data necessitate introducing individual bands I—IV. However, careful examination of several UV patterns presented above, for instance, that given as curve *3* of Fig. 3 as well as those of Figs. 5, 6, and 7, *b* shows that it is impossible to describe these contours using only bands I—IV at any variation of their intensities. This necessitates an introduction into the curve-fitting procedure of a new band V with $\lambda_{max} \approx 340$ nm (see Fig. 8), which can be noticed in some patterns, recorded at temperatures <20 °C, as a shoulder from the high-energy side of band II (see Fig. 3, curve *3* and Fig. 5, curves *5* and *6*). This suggests that one more (the fifth) modification could participate in the complex PT of PDDS.

The results of all the UV experiments show that in spite of the fact that the modifications III and IV are the first and easiest to form from the HCM upon cooling, the most thermodynamically stable is the kinetically hindered modification II. This is not a trivial finding because it is commonly supposed that the most stable should be the *trans* (*all-A*) conformation of the silicon chain stabilized by its maximum σ—σ conjugation evidenced by the greatest red shift of the corresponding UV bands. However, this is not a unique observation since analogous results were obtained by us for other solid poly(dialkylsilanes).[36] This seems to point to the enhanced importance of close packing effects in the crystallization process of some of these polymers.

As for band V, which was revealed as a result of curve-fitting analyses of complicated contours and characterized by values of $\lambda_{max} \approx 340$ nm and $\Delta\nu_{1/2} \approx 2000$ cm^{-1}, this band becomes noticeable in the spectrum only after thermal treatment of the sample and it is difficult to determine its nature. It is pertinent to mention here that an analogous UV band in the same region was noticed previously for a polymer $[(n\text{-Bu})(n\text{-}C_6H_{13})Si]_n$ under particular conditions of PT process[22] and was assigned to an intermediate phase.

Comparative analysis of Raman and UV results

To further identify and characterize the modifications of PDDS participating in the course of complex PT, variable-temperature Raman study of the same samples as were used for the UV measurements was carried out.

The Raman spectrum of PDDS film at ~19 °C depends on the sample thermal prehistory, like the UV spectrum. Figure 9 presents the Raman spectra of the initial polymer sample relaxed for 12 hours at ~19 °C and of the same sample after thermal treatment (annealing). It is important that the Raman spectrum in Fig. 9, curve *1* strictly corresponds to the UV pattern, presented by Fig. 3, curve *2*, while the Raman spectrum in Fig. 9, curve *2* — to the UV pattern in Fig. 3, curve *3*. Both Raman spectra exhibit narrow lines characteristic of the crystalline part of the sample. A very intense narrow line at ~690 cm^{-1} (see Fig. 9, curve *1*) corresponding to the symmetric stretching vibration of the Si—C bonds, ν_s(Si—C), is well-

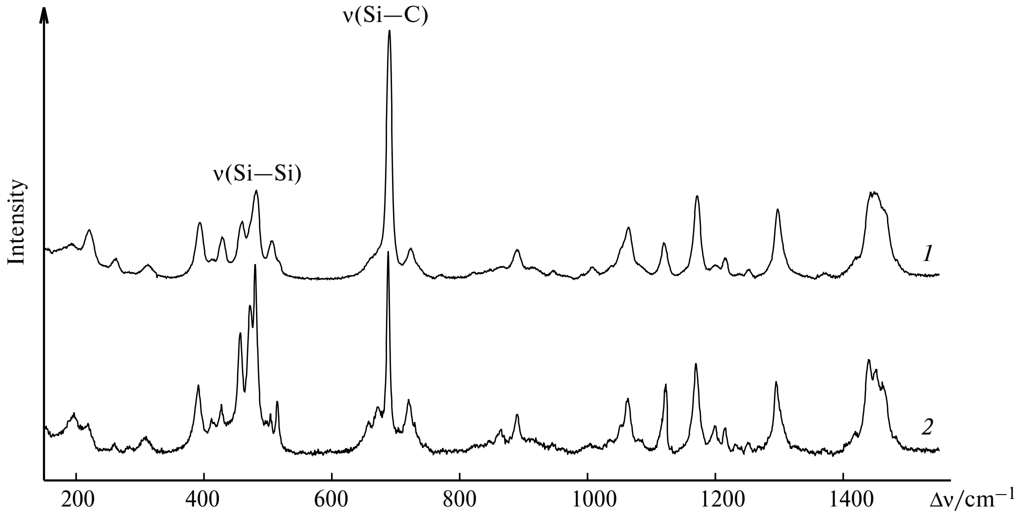

Fig. 9. Raman spectra of PDDS obtained at ~19 °C before (*1*) and after (*2*) annealing.

known to be diagnostic for the polysilane with a planar *trans* (*all-A*) structure of the main chain.[3,22,24b,27b—d,33] However, the pattern of this spectrum observed in the region 350 to 500 cm^{-1} of the stretching vibrations of the Si—Si bonds, ν(Si—Si), is too complicated to be assigned to the *all-A* modification alone. This Raman spectrum as well as the corresponding UV spectrum point to the presence in this sample of another ordered modification.

Annealing of the sample results, first, in Raman line narrowing (see Fig. 9, curve *2*) due to an increase in crystallinity and better resolution, especially in the region 1450 cm^{-1}, and, second, in significant intensity redistribution. In the Raman spectrum of the annealed sample, a narrow ν(Si—Si) line at 480 cm^{-1} becomes comparable in intensity with the most intense "*all*-A" line at 688 cm^{-1}, also appearance of new lines at 197, 519, and 672 cm^{-1} is notable. A comparison of these data with the corresponding UV data shows that these Raman changes are evidently due to an enrichment of the sample with the modification II.

Heating of the sample from ~19 °C to 60 °C results in dramatic changes in the Raman spectrum, presented in Fig. 10 (this process was reflected by the UV patterns given in Fig. 6, *a*, *b*). It is evident, that the process could be divided into two steps. In the interval 20—40 °C (see Fig. 10, curves *1*—*3*), a decrease in intensity of the Raman

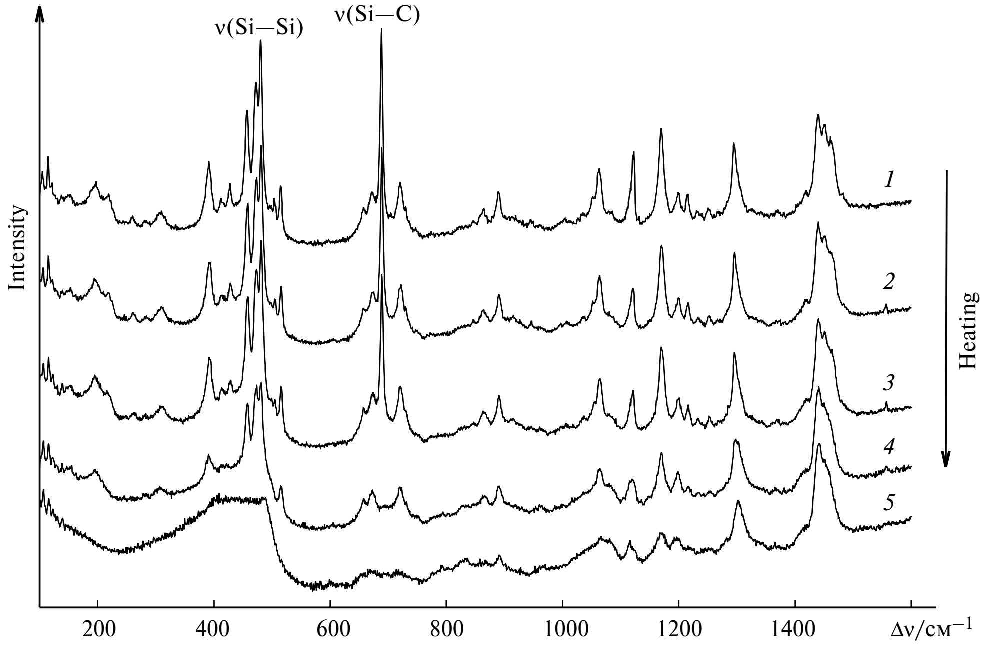

Fig. 10. Temperature evolution of the PDDS Raman spectrum upon heating to 23 (*1*), 30 (*2*), 35 (*3*), 45 (*4*), and 55 °C (*5*).

line at 688 cm^{-1} along with some other lines corresponding to the *all-A* modification is observed. Above 40 °C, they all disappear completely (see Fig. 10, curve *4*). This is in good accord with the UV data and indicates that both overlapping narrow UV bands IV ($\lambda_{max} \approx 380$ nm) and III ($\lambda_{max} \approx 365$ nm) seem to correspond to crystalline modifications with *all-A* or near *all-A* conformations of the macromolecular main chain. An analogous conclusion was made about the same bands in the studies of PT of other poly(dialkylsilanes). This problem was considered in detail using $[(n\text{-}C_6H_{13})_2Si]_n$ as an illustrative example.[39] What is the difference between these two modifications is still a point of discussion. They could differ in effective length of *trans* (*anti)* sequences, in the degree and character of intermolecular ordering[40] or in the values of the dihedral Si—Si—Si—Si angles deviating from 180°. The last point of view is held by the authors.[2a,b,6]

The overall pattern of the Raman spectrum of PDDS film at 45 °C (see Fig. 10, curve *4*) is very close to that presented previously[33] for the *TGTG´* (*AGAG´*) conformation of poly(di-*n*-tetradecylsilane). Thus we could make a conclusion that such a Raman pattern with its most intense narrow line at 480 cm^{-1} together with the UV band with $\lambda_{max} \approx 350$ nm and $\Delta\nu_{1/2} \approx 1200$ cm^{-1} are characteristic of the so-called *AGAG´* conformation of PDDS skeleton in a crystalline phase.

However, it should be noted here that the latter conformation of the silicon chain was suggested[33] for poly(dialkylsilanes) with long alkyl chains on the basis of the wide-angle X-ray diffraction study of poly(di-*n*-tetradecylsilane) which showed a repeat distance along the polymer chain about twice as large as for the *all-A* structure. Molecular mechanics calculations[28b] (though low-level) confirmed the relative stability of such an arrangement. However, in the reviews,[2a,b] this conformation of the polysilane chain is considered as unlikely since this would presumably shift the UV absorption peak to much shorter wavelengths, whereas polysilanes to which this conformation is ascribed, including PDDS, absorb at 350 nm, that is, in the same region as some *transoid* polymers. For this reason, instead of *AGAG´*, an AD_+AD_- arrangement is proposed,[2a,b] which would also fit the observed X-ray data[33] and could account for the $\lambda_{max} \approx$ 350 nm.

Upon heating the sample above 50 °C, all the narrow intense lines disappear and the Raman spectrum becomes weak and blurred, with broad bands in the ν(Si—Si) and ν(Si—C) regions (see Fig. 10, curve *5*), which are typical for HCM with its disordered macromolecular skeleton.

The difference between the T_c values determined in the UV and Raman experiments is evidently due to a small (7—10 °C) warming of the sample in the laser beam.

The conformational state of the long alkyl "tails" could be elucidated on the basis of relative intensities of the Raman lines at 1060 and 1080 cm^{-1}.[8,41,42] The former corresponds to the ν(C—C) mode of *trans* units and the latter to the ν(C—C) mode of *gauche* ones, resulting from hindered rotation about the C—C bonds. In the Raman spectrum of HCM, both lines are of nearly equal intensity (see Fig. 10, curve *5*) and merge into one broad feature. Hence, side chains are conformationally disordered. In the crystalline state the line at 1060 cm^{-1} begins to dominate, which is an evidence of an increase in amount of *trans* units, thus indicating partial ordering of the side groups.

Micromapping of the PDDS film

The results presented above show that in the PDDS film relaxed at room temperature several ordered modifications coexist with different backbone conformations. It was of interest to find out if the film contains separated localities, presenting each individual modification in a pure state. This problem was solved with use of a modern Raman spectrometer equipped with a microscope, which offers surface studies with a spatial resolution better than 3 μm. As a result of the film micromapping, we succeeded in finding micro-regions exhibiting different Raman spectra. As an example, Fig. 11 displays the most informative region of the Raman spectrum (560—760 cm^{-1}) where the lines corresponding to ν(Si—C) stretches are situated, recorded for two different points of the same PDDS sample. The curve *1* evidently corresponds to a pure modi-

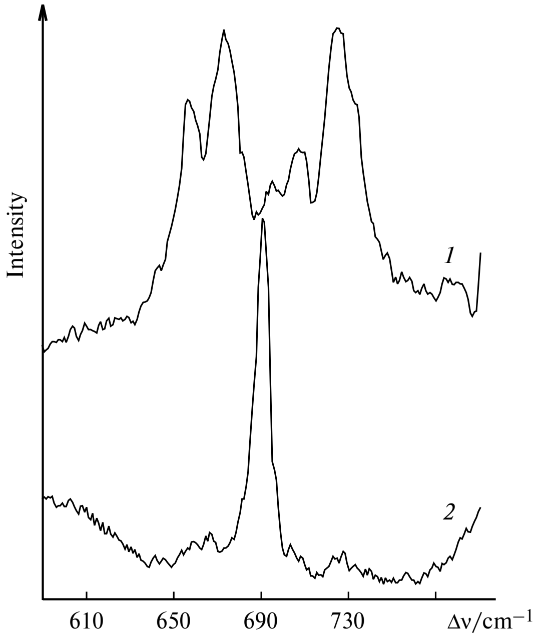

Fig. 11. The Raman spectra (in the ν(Si—C) region) recorded for two different micro-regions of the PDDS film as a result of micromapping. The spectrum (*1*) corresponds to individual modification II while the spectrum (*2*) to modifications III and IV.

fication II with the $AD_{+}AD_{-}$ backbone conformation while curve *2* to a pure *all-A* one.

The UV and Raman results combined with DSC data show that the thermochromic PT of order—disorder type in PDDS proceeds in two steps in the temperature interval between T_c (~60 °C) and T_g (~5 °C). Above T_c, the polymer exists as a modification I that represents a HCM with a disordered macromolecular backbone. Modifications II—IV, which appear below T_c, are crystalline. The backbone conformation in modification II is (proposedly) $AD_{+}AD_{-}$, in modification III — *all-A* or *all-T*, in modification IV — *all-A*. Computer curve-fitting analyses of complicated contours in some UV spectra suggest a presence of a fifth (intermediate) modification. On heating the polymer from ~19 °C to T_c, crystalline modifications III and IV disappear first (at ~45 °C) whereas modification II persists up to T_c.

Relative amount of each modification in the temperature interval between T_c and T_g strongly depends on the sample thermal history; thermal treatment conduces to the sample enrichment with kinetically hindered $AD_{+}AD_{-}$ modification II.

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