Raman study of conformational equilibrium in plastic solid dodecamethylcyclohexasilane Si_6Me_{12}

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The temperature dependence of the Raman spectrum of solid dodecamethylcyclohexasilane Si_6Me_{12} has been studied in the temperature interval 20—235 °C. At 72 °C the substance undergoes a phase transition of an «order—disorder» type, from the ordered crystalline modification to the plastic mesophase with isotropic molecular reorientations. This phase transition is accompanied by the appearance of a conformational equilibrium in the solid state. An analogous equilibrium is also observed in a benzene solution, where the concentration of the second conformer is already noticeable at 6 °C.

Key words: polysilanes, phase transition, plastic phase, conformational equilibrium, Raman spectroscopy.

Previously we established the relationship between the character of Raman spectra and the mobility of «globular» molecules in the solid phase.[1,2] In the present work we have applied the approach developed by us to a «globular» molecule of dodecamethylcyclohexasilane (DMCHS), Si_6Me_{12}. According to X-ray diffraction data,[3] at ambient temperature DMCHS exists as a chair conformation and forms an ordered crystalline modification. An examination of the NMR spectrum made it possible to infer,[4] that when heated to 77 °C this substance is transformed to the plastic phase which exists up to the melting point, 253 °C. The Raman spectrum of DMCHS at ambient temperature has been studied in detail; the assignment of the frequencies has been reported.[5,6] We studied the temperature behavior of the Raman spectrum (the range 5—1500 cm^{-1}) of a solid sample in the temperature region between 20 and 235 °C. The results of the study are given in Figs. 1 and 2,*a*.

At ambient temperature the Raman spectrum exhibits low frequency bands at 22 and 32 cm^{-1} associated with the vibrations of the crystal lattice. As the sample is heated, these bands are retained up to 70 °C, their frequencies regularly decreasing by 2—3 cm^{-1}. At 72 °C the pattern of this spectral region abruptly changes (see Fig. 1): instead of the clear phonon spectrum, there appears a wide Rayleigh wing. At this temperature, in conformity with the literature[4] data, a phase transition of the «order—disorder» type obviously occurs, from the ordered crystalline modification to a plastic mesophase. The slight difference between the phase transition temperature measured by us and that given in Ref. 4, may be due to heating of the sample by the laser beam which is difficult to take into account.

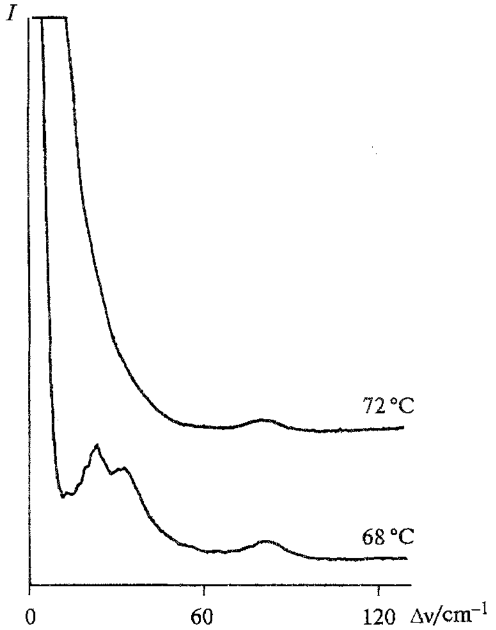

Fig. 1. The manifestation of the phase transition of solid Si_6Me_{12} in the low-frequency region of the Raman spectrum.

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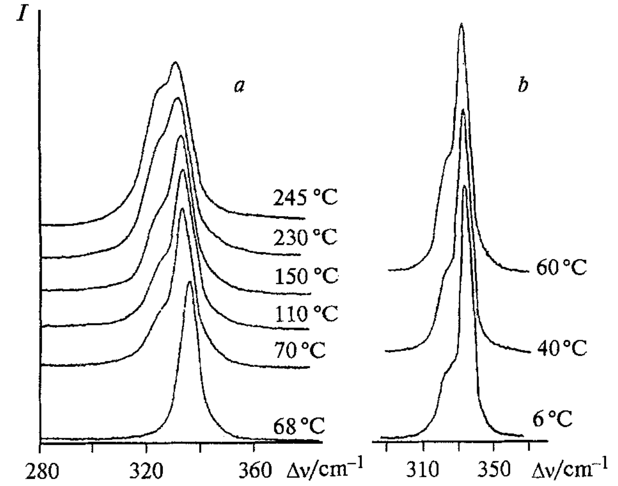

Fig. 2. The temperature dependence of the Raman spectrum of Si_6Me_{12} in the frequency region of the totally symmetrical ν(Si—Si) vibrations of a solid sample (*a*), a solution in benzene (*b*).

With due regard for the criterion developed by us,[1,2] these data imply as well that in the plastic phase of DMHCS (as in the plastic phase of its carbon analog), isotropic reorientations of the molecules whose centers of gravity are fixed in the lattice points occur.

Unexpectedly, it turned out that the phase transition at 72 °C is accompanied not only by the change in the low-frequency region of the spectrum, but also by the appearance of a shoulder at 325 cm^{-1} at the intense line with a frequency of 333 cm^{-1}. The latter is associated with the totally symmetric stretching vibration of the Si—Si bonds in the chair conformation of DMCHS.[5,6] In addition, other changes, although very little, can be observed in the spectrum. For example, a very weak band at 480 cm^{-1} appears in the neighborhood of a weak band at 463 cm^{-1} corresponding to the ν(Si—Si) vibrations of the E_g species. As the temperature is increased, the intensity of the shoulder at 325 cm^{-1} increases (Fig. 2, *a*). The temperature evolution of the spectrum is reversible. We managed to measure the depolarization ratio near the melting point and have shown that the band at 325 cm^{-1} is also polarized, *i.e.*, it is associated with a totally symmetric vibration. These results attest that the second conformation appears, *i.e*, that in the solid state (the plastic phase) the chair conformation is equilibrated with another one (probably a boat and/or a twist conformation) which is less stable and less symmetrical and is manifested as the band at 325 cm^{-1}.

Rotational isomerism caused by hindered rotation about the Si—Si bonds in molecules of polysilanes is well known, however, previously it has only been observed in liquid and gas phases. For example, the results of an electron diffraction study of a related molecule, cyclohexasilane Si_6H_{12}, in vapor at 130 °C have been interpreted[7] as arising from the presence of a mixture of conformers. For a linear molecule, Si_4Me_{10}, it has been shown by ^1H and ^{13}C NMR and Raman spectroscopy[8] that the second conformer appears during melting of the sample; the equilibrium between the *anti*- and *gauche*-conformers in the liquid phase has been studied. In Ref. 8, as in our study, the appearance of the second conformer has been detected by changes in the range 300—500 cm^{-1} of the Raman spectrum, where the ν(Si—Si) stretching vibrations are exhibited: an intense line at 365 cm^{-1}, which corresponds to the totally symmetric ν(Si—Si) vibration of the *anti*-conformer, acquires a shoulder at 355 cm^{-1} which grows with increasing temperature and is associated with the similar vibration of the *gauche*-conformer.

Thus, we have found that the transition of an ordered DMCHS crystal to the solid plastic phase in which molecules have enough room for isotropic reorientation leads simultaneously to the occurrence of rotational isomerism about the Si—Si bonds; *i.e.*, in this case «defrosting» of the external and internal rotation, or more precisely, of the reorientational and conformational degrees of freedom occurs synchronously.

It has also been of interest to elucidate the conformational state of DMCHS in the liquid phase. For this purpose we studied the Raman spectra in the range 300—400 cm^{-1} of a solution of DMCHS in benzene in the temperature region between 5 and 75 °C. The results obtained are given in Fig. 2, *b*, which indicates that in the solution a similar equilibrium is established between the same two conformers with the same ν(Si—Si) frequencies, 333 and 325 cm^{-1}, as in the plastic phase. The proportion of the less stable conformer is quite noticeable even at 6 °C, which implies a small difference between the energies of the two conformers and a low activation barrier, which is in agreement with the literature data.[8—10]

In our opinion, the results obtained may be rather significant for investigating phase transitions of polymeric polydialkylsilanes. These transitions may be both accompanied and not accompanied by a change in the conformation of the main silicon chain. In the former case, changes similar to those found previously[8] and in the present work should apparently be observed in the region of the Raman spectrum characteristic of the ν(Si—Si) vibration frequencies, *viz.*, 350—500 cm^{-1}.

Experimental

DMCHS was prepared according to the modified procedure from Ref. 11. The purity of the compound was checked by NMR, IR absorption, and Raman spectra. To record a Raman spectrum, a sample in a glass capillary was sealed *in vacuo*. The Raman spectra were obtained on RAMANOR HG-2S and U-1000 laser Raman spectrometers with excitation by the 5145 Å line of a ~100 mWt ILA-2 laser. The investigations of the temperature behavior of the spectra were carried out with a capillary containing the sample placed into a specially designed temperature cell. The temperature was maintained with an accuracy of ±1 °C.

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