

# Vibrational and Electronic Spectra and the Structure of Crystalline Poly(dimethylsilane)

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Modern interest in a new class of organosilicon polymers, the polysilanes, is generated by their unique electronic properties,<sup>1</sup> which lead to different applications of possible commercial importance. One of the most intriguing problems in polysilane chemistry is the relation between their conformational structure and electronic spectra. Vibrational spectroscopy, being very sensitive to conformational changes, seems to be an adequate method to solve this problem.

It is reasonable to begin with the simplest representative of the poly(diorganosilane) series, poly(dimethylsilane) (PDMS), which was described as early as in 1949.<sup>2</sup> However, the structure of this crystalline insoluble polymer has not been elucidated. This paper reports the complete vibrational spectrum of PDMS (the Raman spectrum in the region 5–3200 cm<sup>-1</sup> and the IR spectrum in the region 100–3200 cm<sup>-1</sup>) along with its electronic spectrum. These results were briefly published earlier in refs 3 and 4.

The data obtained are presented in Table I and also in Figures 1–3. The vibrational assignment was based upon the analysis of the spectra of related organosilicon compounds<sup>5</sup> and also by analogy with the previous studies of hexamethyldisilane,<sup>6</sup> permethylcyclotrisilanes,<sup>7,8</sup> and linear permethylated tri- and tetrasilanes.<sup>9,10</sup>

It can be seen from the vibrational spectrum of PDMS (Figure 1) that the IR and Raman activities of the skeleton vibrations in the region below 700 cm<sup>-1</sup> are mutually exclusive. This fact is indicative of the centrosymmetric structure of the polymer structural unit. Moreover, in the region 300–500 cm<sup>-1</sup>, characteristic of the Si–Si stretches ( $\nu_{\text{Si-Si}}$ ), Raman lines are observed at 373 and 481 cm<sup>-1</sup>, both having no counterparts in the IR spectrum. Such a picture should be observed only if the silicon backbone of PDMS has a planar trans zigzag conformation (*T<sub>c</sub>*, according to ref 11). In this case the symmetry factor group of the line group of an isolated infinitely long chain molecule is isomorphous with the point group *D*<sub>2h</sub>, and the normal modes of the skeleton structural unit [–SiC<sub>2</sub>–]<sub>2</sub> are distributed among the symmetry species as follows:

$$\Gamma =$$

$$3A_g + 1A_u + 2B_{1g} + 1B_{1u} + 2B_{2g} + 2B_{2u} + 1B_{3g} + 2B_{3u}$$

All the “gerade” species must be active only in the Raman spectrum, and the “ungerade” species only in the IR spectrum, the *A<sub>u</sub>* mode being inactive in both spectra. It is only for this conformation that the two  $\nu_{\text{Si-Si}}$  vibrations, belonging to the *A<sub>g</sub>* and *B<sub>2g</sub>* species, must be both inactive in the IR spectrum.

The Raman lines at 373 and 481 cm<sup>-1</sup> must evidently be assigned to the *A<sub>g</sub>* and *B<sub>2g</sub>* species, respectively, on the basis of the high intensity and the small half-width of the 373-cm<sup>-1</sup> line and the fact that its frequency is close to that of the totally symmetric  $\nu_{\text{Si-Si}}$  stretch of the decamethyltetrasilane trans conformer.<sup>10</sup>

In terms of the PDMS structural unit point symmetry group *D*<sub>2h</sub>, the four Si–C stretching vibrations must belong

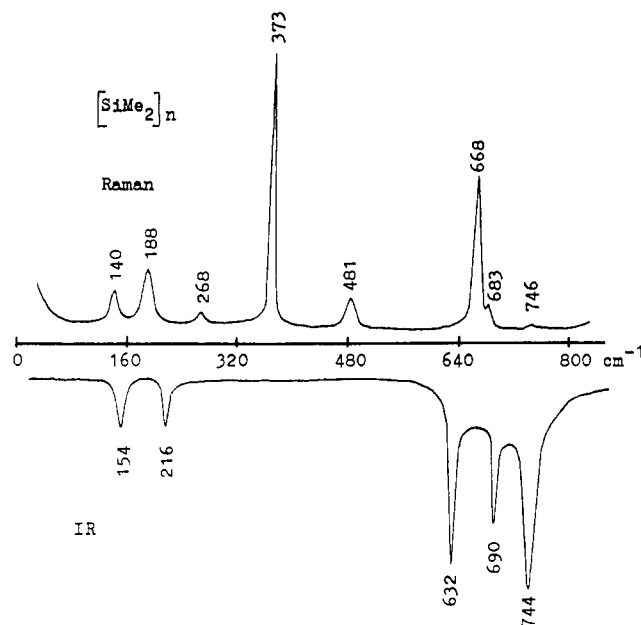


Figure 1. Vibrational spectrum of solid crystalline PDMS at room temperature.

Table I  
Vibrational Assignment of PDMS Spectra

Raman, cm <sup>-1</sup>	IR, cm <sup>-1</sup>	assignment	species
140 (m)			
188 (m)	154 (m)	$\delta_{\text{CSiC}}$	<i>A<sub>g</sub></i>
268 (w)	216 (m)		
373 (vs)		$\nu_{\text{Si-Si}}$	<i>A<sub>g</sub></i>
481 (m)			<i>B<sub>2g</sub></i>
	632 (s)		<i>B<sub>2u</sub> or B<sub>3u</sub></i>
668 (s)		$\nu_{\text{Si-C}}$	<i>A<sub>g</sub></i>
683 (sh)			<i>B<sub>1g</sub></i>
	690 (m)		<i>B<sub>2u</sub> or B<sub>3u</sub></i>
746 (w)	744 (vs)	$\rho\text{CH}_3$	
	832 (s)		
847 (m)			
959 (w)			
1238 (w)	1248 (s)	$\delta_{\text{CH}_3}^s$	
1404 (w)	1404 (m)	$\delta_{\text{CH}_3}^{as}$	
2895 (m)	2896 (m)	$\nu_{\text{CH}_3}^s$	
2956 (m)	2952 (s)	$\nu_{\text{CH}_3}^{as}$	

to the symmetry species  $\Gamma = A_g + B_{1g} + B_{2u} + B_{3u}$ , “gerade” modes being active in the Raman spectrum and “ungerade” in the IR spectrum. Actually, in the region 600–700 cm<sup>-1</sup> we find Raman lines at 668 and 683 cm<sup>-1</sup> and IR bands at 632 and 690 cm<sup>-1</sup>. The high intensity and narrowness of the 668-cm<sup>-1</sup> line make its assignment to the *A<sub>g</sub>* species straightforward. This frequency is close to that of the totally symmetric  $\nu_{\text{Si-C}}$  stretching vibration of *trans*-decamethyltetrasilane.<sup>10</sup> The weak 683-cm<sup>-1</sup> line can therefore be associated with the *B<sub>1g</sub>* species. The assignment of the two  $\nu_{\text{Si-C}}$  IR bands to symmetry species is not possible without normal coordinate treatment. It is notable that the PDMS skeleton vibrational frequencies observed have nothing to do with those predicted for this polymer in ref 12.

The half-widths of the Raman lines belonging to the totally symmetric  $\nu_{\text{Si-Si}}$  and  $\nu_{\text{Si-C}}$  vibrations of PDMS are very small, about 3–4 cm<sup>-1</sup>. These very narrow lines, unusual for a polymer, lead to the conclusion that PDMS is highly ordered, in accordance with X-ray diffraction experimental data.<sup>13,14</sup> Defects of all kinds, including

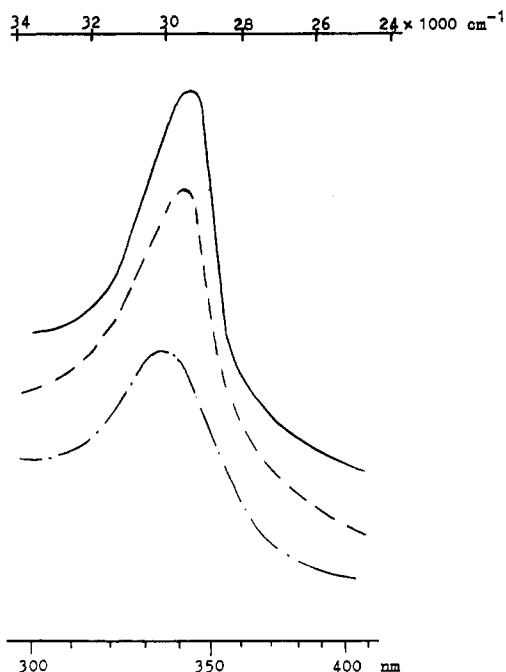


Figure 2. UV absorption spectra of solid crystalline PDMS: (—) 20 °C; (---) 100 °C; (-·-) 160 °C.

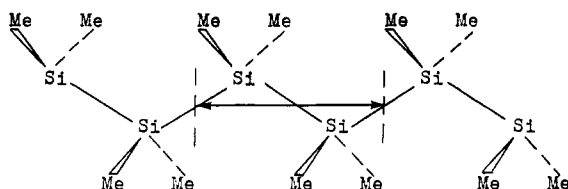


Figure 3. Structure of PDMS in crystal. The structural unit consists of two silicon atoms and four methyl groups.

polymer chain gauche units and the ends of shorter chains, would have led to vibrational dephasing, resulting in broadening of the spectral bands.<sup>15</sup>

The low-frequency vibrations of PDMS (below 350  $\text{cm}^{-1}$ ) are also mutually exclusive. However, they are fewer in number than theory predicts, and there is no basis for an unambiguous assignment. By analogy with the decamethyltetrasilane spectrum,<sup>10</sup> we can associate an intense Raman line at 188  $\text{cm}^{-1}$  with the  $\delta_{\text{CSiC}}$  vibration of the  $A_g$  species. The high intensity of this line may be due to its mixed origin, including participation of the Si-Si and Si-C stretching coordinates.

It is interesting to note that the relative intensity ( $I$ ) of the  $\nu_{\text{Si-Si}}$  and  $\nu_{\text{Si-C}}$  Raman lines, belonging to the  $A_g$  species, strongly depends on the exciting laser line wavelength. A gradual shift of the exciting laser line from the yellow to the blue region of the visible spectrum results in a significant increase of the  $I_{\text{Si-C}}/I_{\text{Si-Si}}$  ratio, thus indicating the preresonance character of the PDMS Raman spectrum.

Internal vibrations of methyl groups attached to a silicon atom have been extensively studied (see ref 5 and references therein). Their assignment in the PDMS spectrum is given by analogy; the methyl group normal modes obey, as usual, the  $C_{3v}$  local symmetry selection rules.

Thus, the most informative part of the PDMS vibrational spectrum is the 350–700- $\text{cm}^{-1}$  region, where the  $\nu_{\text{Si-Si}}$  and  $\nu_{\text{Si-C}}$  stretches are situated. The analysis of this spectral region allowed us to conclude that crystalline PDMS has a planar trans zigzag  $T_\infty$  structure, analogous to that of crystalline polyethylene.<sup>11</sup> Similar conclusions concerning the structure of PDMS have been reported by

Lovinger et al. using a combination of X-ray and electron diffraction and UV spectroscopy.<sup>14</sup> One can find in the literature a number of theoretical predictions of the most stable conformation of an isolated polysilane chain. The results of these calculations strongly depend on the choice of force field. However, they all show that the energy difference between the trans and gauche units is very small (<0.5 kcal/mol). In ref 16, the gauche-helical conformation of PDMS was predicted to be energetically more stable. Perhaps PDMS acquires a planar  $T_\infty$  conformation of the chain in the crystal due to packing favors.

Temperature investigation of the Raman spectrum of PDMS, from ambient temperature to +160 °C, showed no new lines, indicating no changes in the silicon backbone conformation. However, a thorough examination of these results reveals minute changes in the line positions and widths, which will be discussed in subsequent publications.

We have also obtained the UV spectrum of the crystalline PDMS (Figure 2), in which a band at 342 nm was observed. Previously, a correlation was found between the position of the electronic absorption band and the length of the polysilane chain for oligomers with  $n < 200$ . At the value  $n \approx 50$  this curve became parallel to the abscissa with the limiting value of  $\lambda_{\text{max}} \approx 300 \text{ nm}$ .<sup>17</sup> The value 342 nm observed for PDMS in the solid state is much higher. This fact can be rationalized in terms of the high-polymeric nature of our PDMS sample and of the regular planar  $T_\infty$  conformation of the silicon chain, which creates optimal conditions for  $\sigma$ - $\sigma$  conjugation. Heating the sample to 160 °C does not lead to any significant change of the UV spectrum, pointing to the absence of the so-called "thermochromic effect"<sup>1,17</sup> in the conditions studied. Only a slight shift of the band to 334 nm and its broadening are observed, the picture being not reversible. However, IR spectra of PDMS samples after heating in air to 200 °C show the presence of SiOSi bonds due to the partial oxidation of the polymer.

## Experimental Section

PDMS was synthesized by the reaction of dimethyldichlorosilane with sodium in toluene, similar to the procedure in ref 18. Insoluble highly crystalline polymer was purified by exhaustive extraction with hot toluene until the SiOSi band in the IR spectrum disappeared completely.

The Raman spectrum of the solid PDMS in a sealed glass capillary, presented in Figure 1, was obtained using a Ramanor HG-2S laser Raman spectrometer, excited by the 5145-Å line of an ILA-2 Ar<sup>+</sup> laser. The IR spectrum were examined using an M-80 Karl Zeiss spectrophotometer and a Bruker IFS-113 Fourier spectrometer. The samples were either KBr or CsI pellets or Nujol mulls. The UV spectrum of solid PDMS spread between quartz plates was determined with an M-40 Karl Zeiss spectrophotometer.

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- Registry No.** (Me<sub>2</sub>SiCl<sub>2</sub>)<sub>x</sub> (homopolymer), 30107-43-8; (–Si(Me<sub>2</sub>)–)<sub>n</sub> (SRU), 28883-63-8.