Polyvinyl- and polyphenylsilsesquioxanes and their films: an investigation by X-ray diffractometry, positron diagnostics, and ^{29}Si NMR spectroscopy

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Polyvinyl- and polyphenylsilsesquioxanes $(RSiO_{1.5})_n$ were synthesized by hydrolytic polycondensation. The cross section surface areas of the polymer chain were measured and the sizes of "traps" of the free and ordered volumes and the ratio of the T_2 and T_3 units in $(RSiO_{1.5})_n$ were determined by time positron diagnostics, ^{29}Si NMR spectroscopy, and X-ray diffractometry. The density of polyvinyl- and polyphenylsilsesquioxanes was determined picnometrically and from the X-ray phase analysis data, and the content of hydroxyl groups was found by thermogravimetry. The cross section surface area of the silsesquioxane chains containing vinyl and phenyl radicals at Si were calculated by the Miller—Boyer method. The elementary volumes of the chain segments determined by different methods were compared. The geometric models for "traps" of the free volume were proposed. The optical properties and morphology of the polyvinylsilsesquioxane films were studied by atomic force microscopy and UV spectroscopy.

Key words: polyphenylsilsesquioxanes, polyvinylsilsesquioxanes, structure, films, morphology, positron diagnostics.

Polyorganylsilsesquioxanes (POSS) are a well studied class of organosilicon compounds,[1—5] since they possess valuable physical and technical properties.[6—8]

The formation of ladder POSS represents a rare example of the transformation of cage-like polycyclic structures into a ladder macromolecular chain. Along with ladder polyphenylsilsesquioxane,[1] a series of ladder polyalkyl(aryl)silsesquioxanes was synthesized.[4] The general mechanism of formation of these polymers is shown in Scheme 1 and was confirmed by Tikhonov et al.[5]

However, a mixture of ladder branched and cyclic silsesquioxanes was formed already upon the isolation of polymer after the hydrolysis of $RSiCl_3$. It is most likely that hydrolytic polycondensation of $RSiCl_3$ gives intermediate products of *cis*-hydrolysis, *viz.*, cyclic siloxanols,[5] which can be condensed rather easily to form a *cis*-syndiotactic ladder polymer and a branched polymer due to *trans*-tetrols (Scheme 2).
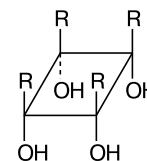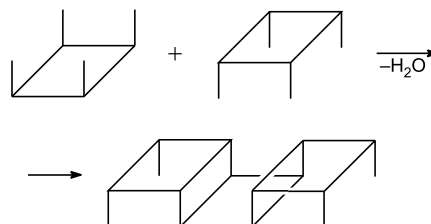

Scheme 1
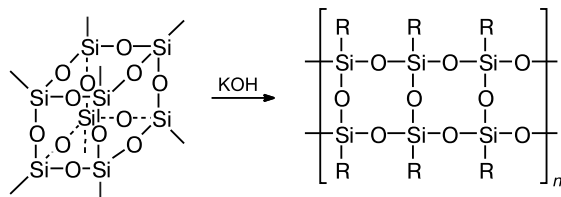
Scheme 2

Table 1. Polymers based on phenyltrichlorosilane and vinyltrichlorosilane

Polymer[a] (fraction)	Elementary unit	n	$\dfrac{\text{Found}}{\text{Calculated}}$ (%)			Yield (%)	d^b/Å	ρ^c /g cm^{-3}
			Si	C	H			
1 (*1*)	$[\text{PhSiO}_{1.5}]_n$	8—15	<u>22.0</u> 21.7	<u>48.6</u> 55.8	<u>4.1</u> 3.9	16.7	14.8	—
1 (*2*)	$[\text{PhSiO}_{1.5}]_n$	34—36	<u>22.9</u> —	<u>55.1</u> —	<u>4.1</u> —	83.3	15.2	1.111
2 (*1*)	$[\text{VinSiO}_{1.5}]_n$	8—15	<u>34.8</u> 35.4	<u>—</u> 30.4	<u>—</u> 4.0	17.6	11.5	—
2 (*2*)	$[\text{VinSiO}_{1.5}]_n$	50—52	<u>35.6</u> —	—	—	82.4	11.2	1.264

[a] Here and in Tables 2—5, 7, and 8, the numbers *1* and *2* denote the low- and high-molecular-weight fraction, respectively.
[b] The Bragg distance obtained from the X-ray diffraction data for the polymers.
[c] The density of the polymers.

A similar mechanism was proposed by Brown[1] in 1963 and considered almost two decades after by Lavrent´ev and Voronkov, whose concepts[7] contradict the accepted structure of these polymers.[9]

In the present work, we used positron diagnostics to study polyphenylsilsesquioxanes (PPSS, **1**) and polyvinyl-sisesquioxanes (PVSS, **2**) synthesized by hydrolytic poly-condensation[10] followed by fractionation into low-molecular-weight fraction *1* and high-molecular-weight fraction *2* (Table 1).

The results of the positron diagnostics study of the synthesized polymers are given in Table 2.

According to the GPC data, the high-molecular-weight fractions of the polymers contain no low-molecular-weight octa-, deca-, and dodecasilsesquioxanes.

Based on the density of PPSS and PVSS, we calculated the number of volumes of the elementary units of these polymers in 1 cm^3

$$N_{\text{RSiO}_{1.5}} = \rho N_A/M, \tag{1}$$

where $N_{\text{RSiO1.5}}$ is the number of volumes of the elementary units, ρ is the density of the polymer, N_A is Avogadro´s constant, and M is the weight of the elementary unit of the polymer.

The numbers of volumes obtained from the positron diagnostics data were compared with the calculated values. The results are presented in Table 3.

The data in Table 3 suggest that the positronium anni-hilation intensity (g_3) depends weakly on the nature of the radical at the Si atom, as indicated by the small change in J_3, being determined by the structure of the polymer chains. At the same time, the positron annihilation intensity (J_2) depends on the nature of the radical at the Si atom; name-ly, it is higher for PVSS containing a more electronegative vinyl radical compared to the phenyl radical in PPSS (see Table 3).

These results are also confirmed by the data of ^{29}Si NMR spectroscopy and thermogravimetric analysis (TGA) of PPSS (fraction *2*) and PVSS (fraction *2*). The ^{29}Si NMR spectra of polymers **1** and **2** exhibit two signals corre-sponding to the units T_2 and T_3. The intensities of these signals differ: for PPSS 30% T_3 and 70% T_2, and for PVSS

**Table 2.** Positron diagnostics data for polymers **1** and **2**

Parameter	Value for the polymer fraction			
	1 (*1*)	**1** (*2*)	**2** (*1*)	**2** (*2*)
τ_1	161.4	169.9	125.1	131.5
J_1	89.29	87.93	82.25	80.13
τ_2	336.50	304.80	284.01	311.80
J_2	6.99	6.90	12.45	12.91
τ_3	1279.7	1372.6	929.7	1349.7
J_3	3.72	5.17	5.29	6.96
K_2	22.53	17.95	55.70	56.77
K_3	20.16	26.63	36.63	47.79
V_{e+}	0.202	0.274	0.397	0.514
V_{ps}	0.164	0.133	0.350	0.432
R_{ps}	5.013	5.029	5.683	5.276
R_{e+}	4.343	4.369	4.438	4.339
$N_{ps} \cdot 10^{22}$/cm^{-1}	0.705	0.963	1.781	1.988
$N_{e+} \cdot 10^{22}$/cm^{-1}	0.429	0.352	0.957	1.129
υ_{ps}	0.134	0.181	0.232	0.323
υ_{e+}	0.125	0.101	0.261	0.330

Note. τ_1 and J_1 are the lifetime and annihilation intensity of different states of positron and positronium (the so-called first component of the positron annihilation spectrum); τ_2 and J_2 are the lifetime and annihilation intensity of positron, respectively; τ_3 and J_3 are the lifetime and annihilation intensity of positroni-um, respectively; K_2 and K_3 are the rates of the interaction with the medium for positron and positronium, respectively; V is the annihilation rate; R is the "trap" radius; N is the number of anni-hilation acts in 1 cm^3; υ is the "trap" volume; e$^+$ is positron; and ps is positronium.

Table 3. Ratio of the number of elementary units to the number of traps in 1 cm³ and the annihilation intensity of positron and positronium

Polymer (fraction)	$N_{RSiO_{1.5}}/N_{ps}$	J_3	$N_{RSiO_{1.5}}/N_{e+}$	J_2
1 (*2*)	3.0	5.17	3.0	6.9
2 (*2*)	3.0	6.96	5.0	12.9

66% T_3 and 33% T_2. The shift is approximately 10 ppm, which is consistent with the published data.[11,12]

$$
\begin{array}{cc}
\underset{|}{R} & \underset{|}{R} \\
O{-}\underset{|}{Si}{-}O & O{-}\underset{|}{Si}{-}O \\
OH & O \\
T_2 & T_3
\end{array}
$$
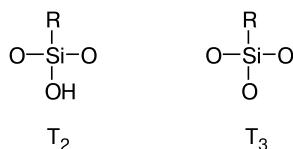
According to the TGA data, the content of hydroxyl groups is 6.25% for PPSS (fraction *2*) and 5.65% for PVSS (fraction *2*). Thus, the empirical formulas presented in Table 4 correspond to the elementary units of PPSS and PVSS.

A comparison of the data in Tables 3 and 4 suggests that the positron interacts with oxygen in the T_2 unit because it is sterically more opened than the T_3 unit.

Using the data in Table 2, we calculated the elementary volumes, where the annihilation of positron (υ_{e+}) and positronium (υ_{comp}) occurs, for polymers **1** (fraction *2*) and **2** (fraction *2*).

The calculations were performed assuming that the fraction of the occupied volume of each component is referred to 1 cm³

$$\upsilon_{comp} = \upsilon_{ps} \cdot 100/(\upsilon_{ps} + \upsilon_{e+}), \qquad (2)$$

and the elementary volume of each component (trap volume) is

$$\upsilon''_{ps} = 1\ \text{см}^3 \cdot \upsilon_{comp}/(N_{ps} \cdot 10^{22}\ \text{cm}^3). \qquad (3)$$

The results obtained are listed in Table 5.

Thus, we showed that the values of τ_2, J_2, and υ_{e+} characterize the internal volumes of structural units of the silsesquioxane polymer chain.

For comparison, we calculated the elementary unit volume from X-ray diffraction (XRD) data. First the cross section surface area of the silsesquioxane chain was calculated from the X-ray phase analysis data by the method described earlier,[13,14] its value was multiplied by the Si—O—Si distance to obtain the desired volume.

The models of polymers chains of PPSS and PVSS were constructed to determine the cross section surface area. The geometric characteristics of the silsesquioxane chain $RSiO_{1.5}$ were taken as a basis.[15,16]

By analyzing the position of the first peak in the curve of X-ray scattering from amorphous polymers one can obtain information on the short-range order in the structure without detailed modeling of the structures of particular units and their mutual arrangement.[13,14] Applying the Bragg equation $\lambda = 2d\sin\theta$ (where λ is the wavelength of scattered radiation and θ is the scattering angle) to the first maximum, one gets a parameter d characterizing the structure of the polymer chain. The d value correlates with the cross section surface area of the polymer chain. The relationship between the cross section surface area and the position of the first peak in the diffraction curve is given by

$$\log d = k_1 + k_2 \log s, \qquad (4)$$

where s is the cross section surface area, d is the "interplanar distance" obtained as a result of application of the Bragg equation to the first peak position, and k_1 and k_2 are coefficients.

This equation represents a straight line equation in the coordinates $\log s$—$\log d$ with the cross section surface area being a parameter characterizing the chain packing. The square root of the cross section surface area is the effective thickness of the chain (inter-chain distance).

All polymers analyzed earlier[16] can be divided into three groups described by three straight lines in the plot $\log d = f \log s$ (Fig. 1).

Thus, the "interplanar spacing" d determined by the position of the first maximum in the X-ray scattering curve is an objective parameter that can be used to describe the structure of amorphous polymers. Here the cross section surface area of the chain (s) related to the value of d by Eq.(4) serves as a structural parameter.

Table 4. Signal intensities of T_2 and T_3 units and the content of hydroxyl groups in the elementary units of PPSS and PVSS

Polymer (fraction)	T_2	T_3	Elementary unit	Content of OH groups, found / calculated (%)
	%			
1 (*2*)	70.0	30.0	$[(PhSiO_{1.5})_2(PhSi(OH)O)_7]_n$	6.25 / 6.30
2 (*2*)	33.0	66.0	$[(VinSiO_{1.5})_2VinSi(OH)O]_n$	5.60 / 6.90

Table 5. Results of calculation of the elementary volumes of the "traps" in PPSS and PVSS

Polymer (fraction)	$\upsilon_{ps}/\text{Å}^3$	τ_3	$N_{ps}\cdot 10^{22}/\text{cm}^{-1}$	$\upsilon_{e+}/\text{Å}^3$	τ_2	$N_{e+}\cdot 10^{22}/\text{cm}^{-1}$
1 (*2*)	420.0	1372.6	0.181	257.0	304	0.101
2 (*2*)	197.0	1349.7	0.323	110.6	311	0.330

The values of the cross section surface area of the polymer chain obtained from an analysis of the first peak of the X-ray scattering curve were compared with those calculated from the structural model. The results of studies[15,16] of crystalline cyclic silsesquioxanes (Fig. 2, *a*) were taken as a basis for modeling of the structure of amorphous polymers. The elementary unit of the PPSS structure is a tetra-silsesquioxane cycle. The Si atoms occupy vertices of a cube with an edge of 0.317 nm.

In the polymer, the cyclic fragment (see Fig. 2, *a*) is transformed into the open-chain fragment (see Fig. 2, *b*) due to the inflection of the reference cycles along the t—t line, which is accompanied by an increase in the dihedral angle to 108°. The cross section of the molecule is a rectangle whose vertices are occupied by C atoms. The cross section surface area (with allowance for the size of the C atom) is 1.088 nm^2 for PPSS and 0.775 nm^2 for PVSS.

The cross section surface areas of the PPSS and PVSS polymer chains are presented in Table 7; the parameter d
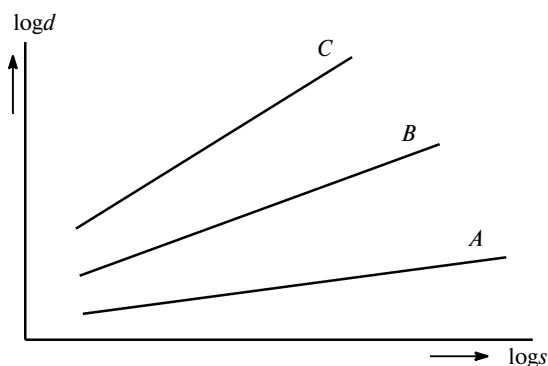

Fig. 1. Logarithm of the interplanar distance (*d*) *vs* logarithm of the cross section surface (*s*) for polymers of diverse nature.

Fig. 2. Cyclic (*a*) and open-chain (*b*) conformations of the silsesquioxane chain.

characterizes the "interplanar distance" determined by the position of the first maximum of the X-ray scattering curve. The values of ΔA, ΔB, and ΔC represent the deviations of the log$d$ values from the straight line specified by the coefficients k_1 and k_2 (see Table 6); s_A, s_B, and s_C are the surface areas calculated by the equation log$d = k_1 + k_2$log$s$ with the coefficients k_1 and k_2 corresponding to the lines A, B, and C. The results show that the samples under study belong to type B.

Thus, the structures of these polymers agree with the data obtained by Voronkov and Lavrent´ev[7] and reject the commonly accepted structures proposed earlier.[9]

The results obtained made it possible to calculate the interchain volumes (Table 8), which are formed upon the shift along the axis and displacement of the silsesquioxane chains, because the internal volumes of the silsesquioxane chains (see Fig. 2, *b*) are smaller than 40 Å^3. The estimates of the interchain volumes are shown in Fig. 3.

To understand more clearly the volume of the polymer chain in which positron annihilation occurs, we calculated the elementary unit volumes of PPSS and PVSS based on the published data,[15,16] on the results of the X-ray diffraction study of PPSS (fraction *2*) and PVSS (fraction *2*) determined by the earlier described methods,[13,14] the values of density, and from the positron diagnostics (PD) data (see Table 8).

We analyzed in which region of interchain interaction does positronium annihilation (τ_3, J_3) occur. For this purpose, we calculated the possible empty volumes between close-packed stacks of organylsilsesquioxane chains.

The elementary unit volumes ($\upsilon_{el.un}$) were calculated from the density as follows:

$$\upsilon_{el.un} = MN/(\rho N_A), \tag{8}$$

$$\upsilon_{el.un} = M\cdot 10^{24}/[1.26 \text{ g cm}^{-3}\cdot(6.03\cdot 10^{23})],$$

Table 6. Values of coefficients k_1 and k_2 in Eq. (4)* and the calculated correlation coefficient R^2

Straight line in Fig. 1	k_1	k_2	R^2
A	−0.31	0.20	0.719
B	0.06	0.61	0.971
C	0.53	0.90	0.931

* Published data.[13,14]
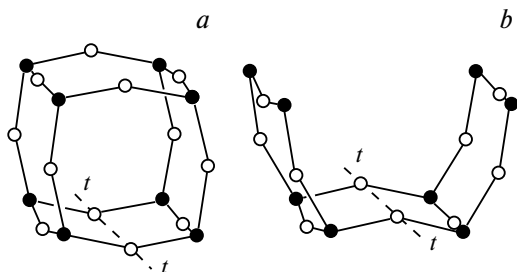
Table 7. Cross section surface areas of the polymer chains of PPSS and PVSS calculated by the Miller—Boyer[13,14] method

Polymer (fraction)	Surface area/nm^2	d/nm	ΔA	ΔB	ΔC	s_A	s_B	s_C
1 (*2*)	1.088	1.20	0.382	0.00322	0.484	88.289	1.0751	0.3155
2 (*2*)	0.775	0.98	0.323	0.00118	0.439	32.072	0.7713	0.2520

a   *b*

$\upsilon_1 = 194$ Å^3
$\upsilon_2 = 114$ Å^3
$\upsilon_3 = 154$ Å^3
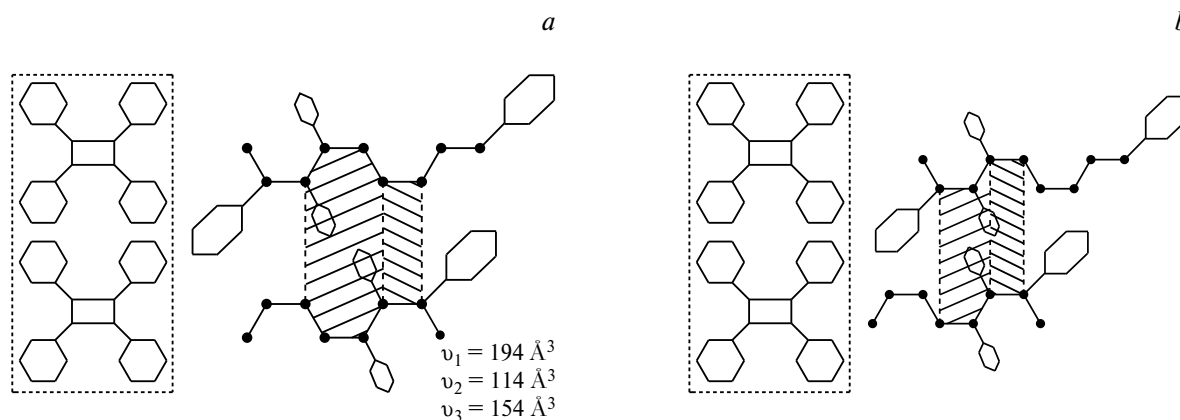
Fig. 3. Arrangement of silsesquioxane chains relative to each other: *a*, radicals are located above radicals, and *b*, shift along the chain by 0.5 of the silsesquioxane fragment.

where M is the weight of the elementary unit, N_A is Avogadro´s constant, ρ is the density of the polymer, and N is the number of the elementary unit volumes (Å^3) per cubic centimeter.

The shift by one (RSiO$_{1.5}$)$_8$ unit results in the formation of rather large volumes of the interchain space (Fig. 4).

A comparison of the results of calculations (Table 9) and the positron diagnostics data suggests where the annihilation "traps" for positron n(e$^+$) and positronium (ps) are formed.

Thus, it can be concluded that positronium (lifetime τ_3) annihilates in the "trap" whose average volume is 460 Å^3. This corresponds to the volumes localized between stacks of silsesquioxane chains, *i.e.*, to the volumes of the disordered "supramolecular" structure. Positron (lifetime τ_2) annihilates in the volume between the chains in a

stack (114—190 Å^3 depending on the size of the radical, see Table 8).

Polyorganylsilsesquioxanes with a high refractive index, high resistance to the environment, a low absorption coefficient, and good adhesive properties are used for the formation of basis components of vacuum lithography.[17]
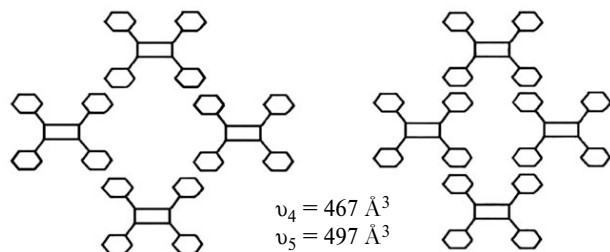
We obtained films on sodium-silicate glass and mica by "molecular deposition" of VinSiCl$_3$ using hydrolytic polycondensation.[18]

Table 8. Elementary unit volumes for PPSS and PVSS

Polymer (fraction)	υ/Å^3, calculated		υ/Å^3, found	
	from ρ	from XRD data	from ρ_{exp}	from PD data
1 (*2*)	95.3	95.2	103.9	110.0
2 (*2*)	164.6	173.0	192.7	257.0

$\upsilon_4 = 467$ Å^3
$\upsilon_5 = 497$ Å^3

Fig. 4. Geometry of silsesquioxane chains with various spatial arrangements.

Table 9. Geometric sizes of assumed voids inside the silsesquioxane chains and between them

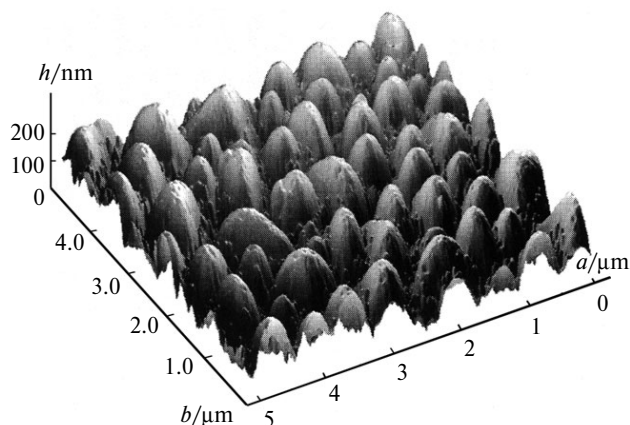| Poly-mer	υ_1	υ_2	υ_3	υ_{e+}	υ_{ps}	υ_4
				Å^3		
1	194	114	154	257.0	420.0	467—492
2	179	95	128	110.0	197.0	310—366

Fig. 5. AFM image of the surface of the polyvinylsilsesquioxane film.

A globular structure is observed on the surface of the polyvinylsilsesquioxane film (fraction *2*) deposited on glass (Fig. 5). The average height of globules is 150—200 nm, the distance between vertices of the globules is 0.8—1.5 μm, and the measured thickness value is 1.6 μm.

The spectrum of the polyvinylsilsesquioxane film presented in Fig. 6 indicates that the film possesses total internal reflection in the range λ = 300—900 nm.

The results obtained show that the polyvinylsilsesquioxane films are nanostructured media with a high refractive index and are appropriate for waveguide applications.

Experimental

The lifetimes of positrons (τ_2) and positronium (τ_3) in the polymers were measured on a fast-fast delayed coincidence circuit spectrometer using scintillation plastic detectors 25×15 mm in diameter and FEU-87 based on a NOKIA-LP-4840 analyzer.[19] Fast electronics units were produced by the methods described earlier.[20] The time resolution of the spectrometer ($2\tau_0$) was 270 ps for the ^{60}Co source at the 30% width of the energy "window." A cyclotron ^{44}Ti source with an activity of 10—15 mCi was used for measuring the positron lifetimes. The time-resolved spectra were processed by the PALFIT program.[19]
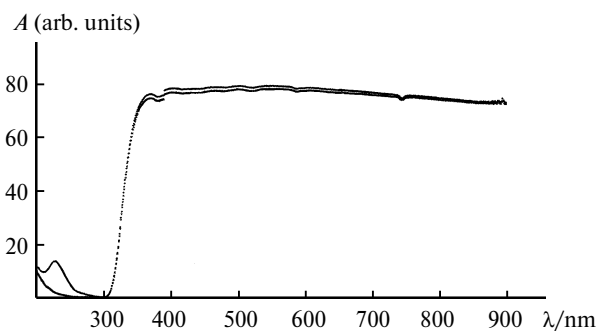

Fig. 6. Total internal reflection spectrum of polyvinylsilsesquioxane film in the UV and visible regions.

Thermogravimetric analysis was carried out on a Mettler Toledo TGA/DSC1 derivatograph with a heating rate of 10 °C min^{-1} in air. The solid state ^{29}Si NMR spectra were recorded by the polarization transfer from hydrogen nuclei and magic angle spinning on a Bruker MSL-400 spectrometer at a spinning rate of 4 kHz. The structure of the surface of the polyvinylsilsesquioxane film (fraction *2*) was studied with an NTMDT Solver P46 atomic force microscope. The reflectance spectra in the UV and visible regions were recorded on a Hitachi U2010 spectrophotometer. The densities of polysilsesquioxanes were determined picnometrically in anhydrous hexadecane.

Polivinyl- and polyphenylsilsesquioxanes were synthesized by the hydrolysis of PhSiCl$_3$ and VinSiCl$_3$, respectively, in an aqueous-ether medium.[10]

Polyphenylsilsesquioxane. To a cooled mixture of sulfuric ether (150 mL) and water (250 mL), a solution of phenyltrichlorosilane (0.5 mol, 106 g, 83 mL) in sulfuric ether (150 mL) was added dropwise with stirring, maintaining continuous boiling. The organic layer was separated and the aqueous layer was extracted with sulfuric ether (3×50 mL). The ethereal extracts were combined, the ether was distilled off, and the resin was dried to a constant weight at 80 °C (20 Torr). The yield of the product and the elemental analysis data are given in Table 1.

Polyvinylsilsesquioxane was synthesized similarly to polyphenylsilsesquioxane. The yield of the product and the elemental analysis data are given in Table 1.

The molecular weight was determined and the synthesized polymers were separated into the low- and high-molecular-weight fractions by gel permeation chromatography on a styrene—divinylbenzene (4%) copolymer in a column (1800×20 mm) using toluene as an eluent (grain diameter 0.15—0.30 mm, degree of swelling in toluene 1.3; the free volume of the column was 65 mL).

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