1402 *Russian Chemical Bulletin, International Edition, Vol. 56, No. 7, pp. 1402—1407, July, 2007*

Synthesis and mesomorphic properties of *cis*-penta[(phenyl)(trimethylsiloxy)]cyclopentasiloxane

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New stereoregular *cis*-penta[(phenyl)(trimethylsiloxy)]cyclopentasiloxane *cis*-$[PhSi(O)(OSiMe_3)]_5$ was synthesized. According to the data from DSC, X-ray diffraction, and polarization microscopy, the noncrystallizable cyclopentasiloxane exists in the mesomorphic state throughout the temperature range below the temperature of destruction and is transformed into mesomorphic glass below the glass transition temperature. This compound possesses the polymesomorphic properties and forms two mesomorphic modifications. The type of mesomorphic ordering for these modifications was determined.

Key words: polyhedral metallasiloxanes, trimethylsilylation, stereoregular organocyclosiloxanes, mesomorphic state, polymesomorphism, phase transitions, plastic crystals, differential scanning calorimetry, X-ray diffraction study, polarization microscopy.

Earlier,[1—11] we have demonstrated that polyhedral organometallasiloxanes (OMS) can be used for the synthesis of a new class of stereoregular organocyclosiloxanes. A procedure for the synthesis of the starting OMS is based on the hydrolytic condensation of organotrialkoxysilanes, which occurs with the involvement of various metal ions to give the cyclic organosiloxanolate ligand $[RSi(O)O^-]_n$ on a metal ion matrix. The size and configuration of the cyclic ligand $[RSi(O)O^-]_n$ depend primarily on the nature of metal. The removal of metal ions by triorganylchlorosilanes or dilute HCl allows the isolation of the cyclic organosiloxanolate fragment in the form of its triorganylsiloxy or hydroxy derivative. Studies of the physical properties of cyclosiloxanes showed[3—11] that almost all these compounds exhibit the mesomorphic properties in a wide temperature range.

We have also demonstrated[3,4,6,7] that organocyclosiloxanes (OSC) of the general formula *cis*-$[PhSi(O)(OSiMe_2R)]_n$ (n = 4 or 6; R = Me, CH_2Cl, or $HC{=}CH_2$), which were synthesized from the corresponding metallasiloxanes, are transformed into the mesomorphic state above the melting point of the crystalline phase. It was found[3,4] that all cyclotetrasiloxanes with $n = 4$ ($\mathbf{D}_4$) form 3D plastic-crystalline mesophases regardless of the structure of the side groups R. In 3D mesophases, molecules of all compounds $\mathbf{D}_4$ occupy the body-centered cubic (BCC) lattice points.[3,4] The mesomorphic properties change substantially as the size of the siloxane ring increases to $n = 6$, *i.e.*, in cyclohexasiloxanes ($\mathbf{D}_6$).[6,7] Compounds $\mathbf{D}_6$ are prone to polymesomorphism and form two mesomorphic modifications, which differ in the dimensionality of the order and the type of ordering. Immediately after melting of the crystalline phase, cyclohexasiloxanes form a 2D-type columnar hexagonal mesophase (low-temperature (LT) mesophase). The rise of the temperature causes the polymesomorphic transition of the LT mesophase to the high-temperature (HT) mesophase. The HT mesophase is characterized by the higher order (3D), and its structural organization is typical of plastic crystals. The above-mentioned features of the mesomorphism of these cyclohexasiloxanes are observed regardless of the nature of the side groups R. A change in the chemical structure of these groups in compounds $\mathbf{D}_4$ and $\mathbf{D}_6$ has no effect on the structural organization of the mesophase.[3,4,6,7] At the same time, the temperature range of the existence of 3D and 2D mesophases and the unit cell parameters of plastic crystals and columnar mesophases substantially depend on the nature of the side substituents.[7]

Therefore, for a series of compounds under consideration, the ring size is the factor controlling the structural organization of the mesophase and the tendency to polymesomorphism. In this connection, it was of interest to study the compound occupying the intermediate position between $\mathbf{D}_4$ and $\mathbf{D}_6$, *viz.*, cyclopentasiloxane ($\mathbf{D}_5$) *cis*-$[PhSi(O)(OSiMe_2R)]_5$, where R = Me.

Earlier,[12—14] when studying the properties of OMS, we have found that the cyclic organosiloxanolate ligand can undergo rearrangements and the chemical composi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1353—1358, July, 2007.

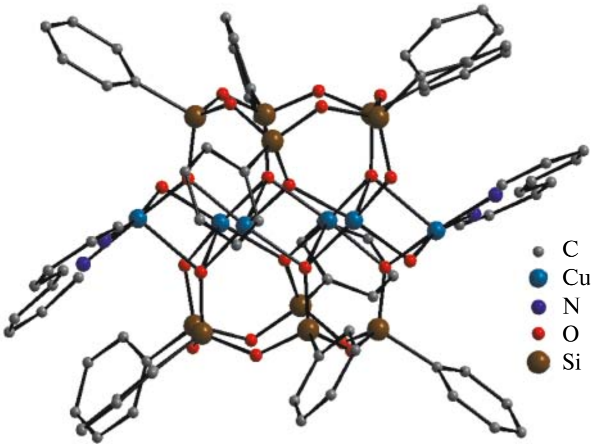
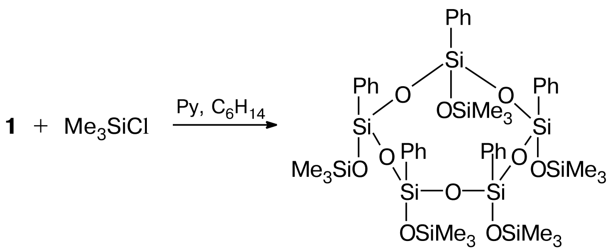


Fig. 1. Molecular structure of compound **1**.
Note. Fig. 1 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

tion of the metallasiloxane molecule can be changed in the presence of strong electron donors. In particular, Cu/Na-phenylsiloxane $\{Na_4[(PhSi(O)O)_{12}Cu_4]\} \cdot 8BuOH$[15] based on the 12-membered ligand tris-*cis*-tris-*trans*-$[PhSi(O)O^-]_{12}$ is rearranged to give another copper complex, *viz*., $\{Cu_6[(PhSi(O)O)_5]_2(OH)_2(C_{10}H_8N_2)_2\} \cdot 4(DMF) \cdot 3H_2O$ (**1**), in DMF in the presence of 2,2´-bipyridyl. The molecule of the latter complex contains two *cis*-cyclopentasiloxanolate ligands *cis*-$[PhSi(O)O^-]_5$ and two 2,2´-bipyridyl molecules coordinated on a matrix consisting of six copper ions (Fig. 1).

In the present study, we synthesized *cis*-penta[(phenyl)(trimethylsiloxy)]cyclopentasiloxane *cis*-$[PhSi(O)(OSiMe_3)]_5$ (**2**) by the reaction of compound **1** with trimethylchlorosilane according to Scheme 1 and investigated the properties of compound **2**.

Scheme 1



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Experimental

Trimethylchlorosilane (Aldrich), pyridine (Aldrich), hexane (reagent grade), and NaOH (analytical grade) were used. Anhydrous $CuCl_2$ was prepared by heating the crystal hydrate at 120 °C to constant weight. The solvents were purified according to known procedures.[16] Compound **1** was synthesized as described earlier.[14]

The ^1H and ^{29}Si NMR spectra were recorded on a Bruker AMX spectrometer (400.1 MHz for ^1H and 79.5 MHz for ^{29}Si) at 20 °C in $CDCl_3$. The DSC measurements were carried out on a Mettler-822e differential scanning calorimeter at a heating/cooling rate of 20 deg min^{-1} under argon. The position of the minimum (maximum) of the peak in the DSC curve was taken as the transition temperature. X-ray diffraction studies were performed on a Dron-3M diffractometer (Cu-Kα radiation, a curved quartz crystal as the point-focusing monochromator) equipped with a high-temperature chamber (temperature was maintained within ±1 °C). The X-ray diffraction patterns were measured in the transmission mode. The optical measurements were performed on a POLAM-213M polarization microscope.

***cis*-Penta[(phenyl)(trimethylsiloxy)]cyclopentasiloxane (2).** Compound **1** (0.6 g, 0.276 mmol) was placed in a flask, pyridine (0.8 mL, 0.79 g, 9.942 mmol) was added, and then a solution of trimethylchlorosilane (1.68 mL, 1.44 g, 13.256 mmol) in hexane (25 mL) was added with stirring. The reaction mixture was refluxed for 1 h, cooled to ~20 °C, and filtered off from the precipitate. The filtrate was washed with water until Cl^- ions disappeared and then dried over Na_2SO_4. The solution was filtered, and the solvent was removed (10 Torr, 50 °C) on a rotary evaporator *in vacuo* (1 Torr, 50 °C). The yield of the waxy white product was 0.45 g (77.6%). Found (%): C, 50.93; H, 6.68; Si, 26.11. $[PhSi(O)(OSiMe_3)]_5$, $C_{45}H_{70}Si_{10}O_{10}$. Calculated (%): C, 51.38; H, 6.71; Si, 26.70.

^1H NMR (Fig. 2), δ: 0.194 (s, 9 H, $OSi(CH_3)_3$); 6.95—7.23 (m, 5 H, $O_3SiC_6H_5$); the integrated intensity ratio of the signals for the protons of $OSi(CH_3)_3$ and $O_3SiC_6H_5$ was 9 : 5. ^{29}Si NMR (see Fig. 2), δ: –81.32 (s, $O_3SiC_6H_5$); 9.99 (s, $OSi(CH_3)_3$).

Results and Discussion

At ~20 °C, compound **2** is waxy and very viscous. To study the optical properties, this compound was placed between two cover slips and pressed to prepare a thin layer. At ~20 °C, compound **2** gives a pronounced honeycomb texture under normal light (Fig. 3, *a*). The birefringence was not observed through crossed polaroids (Fig. 3, *b*). The observed honeycomb texture (see Fig. 3, *a*) is analogous to the so-called Bernard cells, whose appearance is associated with the free convection.[17—19] Earlier, we have found analogous honeycomb textures for a series of plastic crystals of octaphenylcyclotetrasiloxane,[4] **D**$_4$,[4] and their mixtures,[20] as well as for some bifunctional decamethylcyclohexasilanes.[21]

Upon heating to 165 °C, compound **2** possesses the birefringent properties, and the texture is retained in the observations both through crossed polaroids and under normal light (Fig. 3 *b*, *d*) up to its sublimation temperature (365 °C). Hence, compound **2** exists presumably in the plastic-crystalline mesomorphic state at 20 °C (mesophase *1*), and the polymesomorphic transition of this compound occurs at ~165 °C.

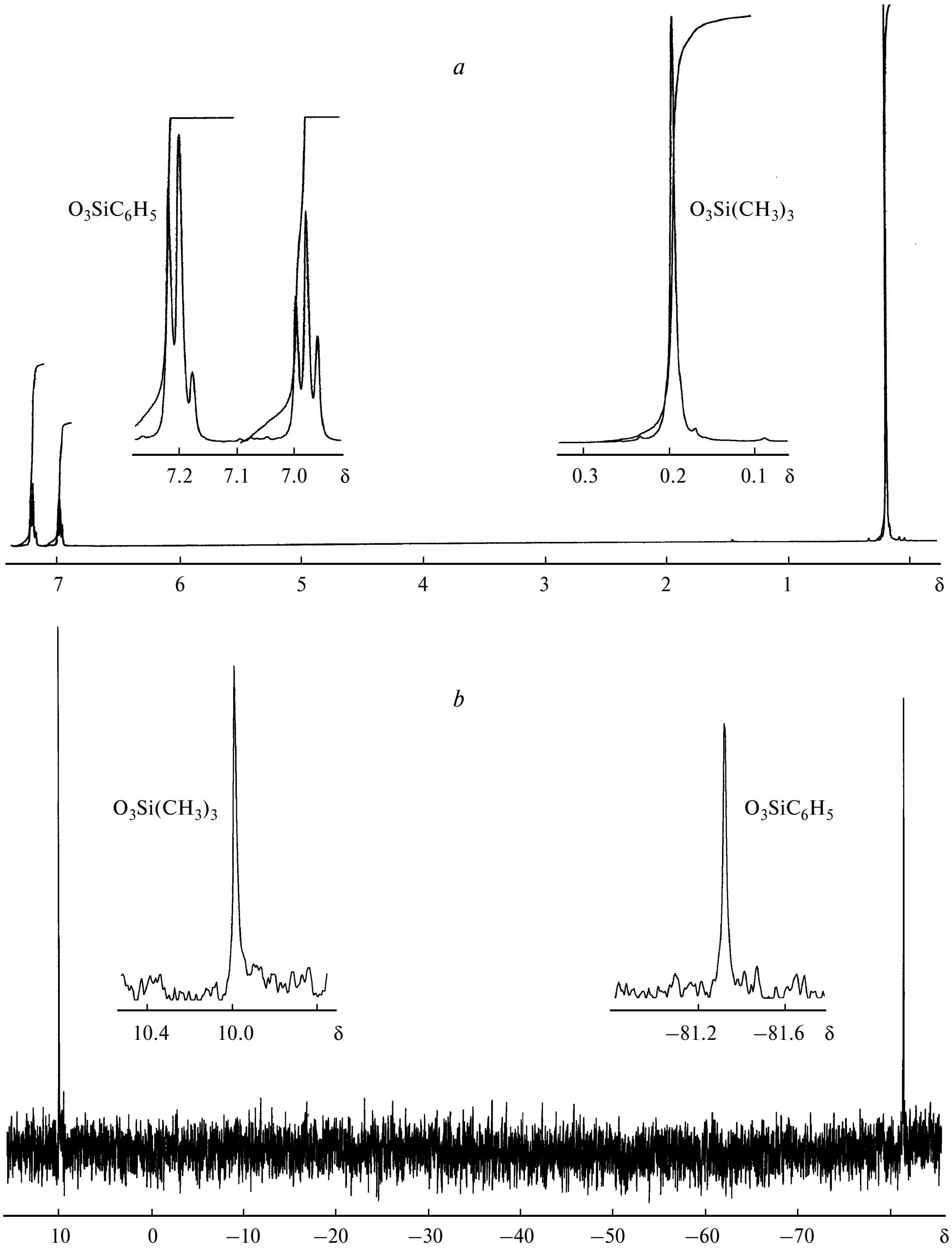

Fig. 2. ^{1}H NMR (*a*) and ^{29}Si NMR (*b*) spectra of compound **2**.

According to the DSC data (Fig. 4), compound **2** does not crystallize. The DSC curves obtained by a heating scan show a heat-capacity jump associated with the devitrification of the plastic-crystalline mesophase at −56 °C ($\Delta C_p = 0.19$ J g^{-1} K^{-1}) and an endothermic peak with a maximum at 164 °C and $\Delta H = 0.9$ J g^{-1} (see Fig. 4). Taking into account the results of polarization microscopy, it can be concluded that the first thermal effect is associated with the devitrification of the plastic-crystalline mesophase, and the second effect, whose temperature coincides with the appearance of the birefringence, is associated with the polymesomorphic transition mesophase *1* → mesophase *2*. The cooling curve shows an exothermic peak at 121 °C and $\Delta H = 0.91$ J g^{-1} corresponding to the transition mesophase *2* → mesophase *1* and a heat capacity jump corresponding to the glass tran-

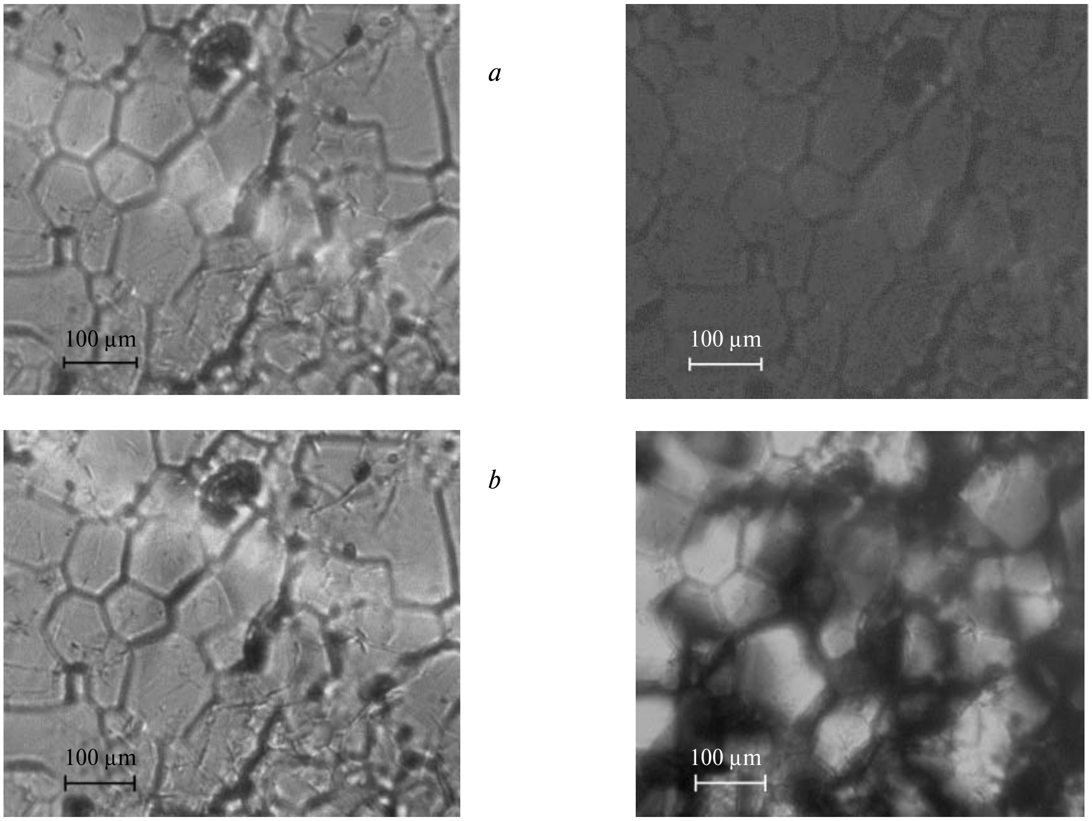

Fig. 3. Transmission micrographs of compound **2** under normal (*a*, *b*) and polarized (*c*, *d*) light at 25 (*a*, *c*) and 200 °C (*b*, *d*).

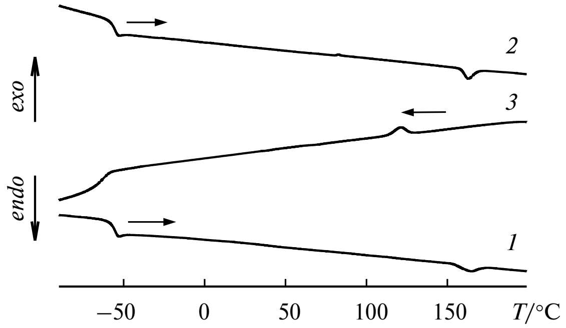

Fig. 4. DSC curves for compound **2** during the first (*1*) and second heating scans (*2*) and the cooling scan (*3*) at a rate of ±20 deg min^{-1} under argon.

sition of mesophase *1* at −69 °C (ΔC_P = 0.19 J g^{-1} K^{-1}). The thermodynamic parameters of the observed transitions both during the first and second heating scans and during the cooling scan remain unchanged. The observed hysteresis of the polymesomorphic phase transition temperature and the glass transition temperature can be attributed to low rates of these transitions, which are manifested at rather high heating—cooling rates.

To confirm these conclusions and to determine the type of ordering of the mesomorphic modifications, we measured X-ray diffraction patterns for compound **2** at different temperatures.

The X-ray diffraction pattern of compound **2** at 20 °C (Fig. 5, *a*) contains five narrow ($\Delta_{1/2}$ = 0.25°) reflections at 2θ = 8.39, 11.88, 14.56, 16.83, and 18.83° and a broad amorphous halo at 2θ = 13—30° with a maximum at 2θ ~18°. This X-ray diffraction pattern is typical of mesomorphic systems. Since $\sin^2\theta$ for the adjacent reflections are in a ratio of 1 : 2 : 3 : 4 : 5, this mesophase can be considered as cubic. This is also evidenced by the optical isotropism of the mesophase at 20 °C (see Fig. 3, *a*). Therefore, the X-ray diffraction data confirm the validity of the assignment of mesophase *1* of compound **2** to plastic crystals. Based on the ratio between $\sin^2\theta$, the reflections can be indexed both in the simple and BCC lattices. However, the packing coefficient *k* calculated assuming the simple cubic lattice was unrealistic.[22] The analogous calculation assuming the body-centered cubic lattice with the unit cell parameter *a* = 14.90 Å (20 °C) gave good results. Actually, the sum of the van der Waals volumes of the atomic increments involved in molecule **2** $\Sigma\Delta V_i$ = 1005.7 Å^3, and the volume of the BCC unit cell at 20 °C *V* = 3307.95 Å^3, which corresponds to *k* ~0.61. In this case, the observed reflections should be indexed as 110, 200, 211, 220, and 310.

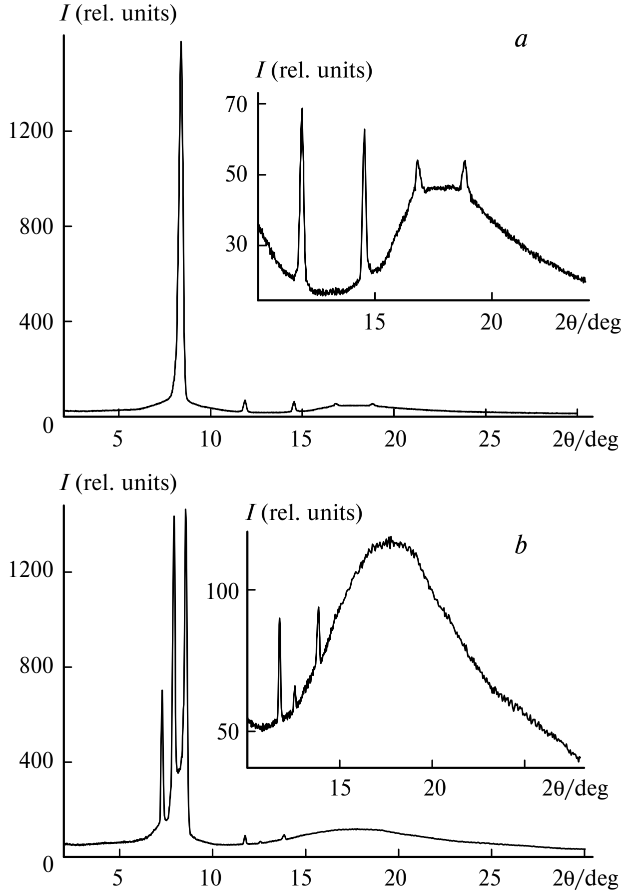

Fig. 5. X-ray diffraction patterns of compound **2** at 20 (*a*) and 178 °C (*b*).

The rise of the temperature leads to a substantial shift of the angular positions of reflections toward smaller values and a decrease in the number of reflections, which is typical for mesomorphic systems, including plastic crystals. For example, the X-ray diffraction pattern measured at 110 °C contains only three reflections at $2\theta = 8.21$, 11.62, and 14.24°, which corresponds to an increase in the unit cell parameter a of the BCC lattice to 15.23 Å and a decrease in the packing coefficient k to 0.57. At 140 °C, the X-ray diffraction pattern contains only two reflections at $2\theta = 8.12$ and 11.49°, and the parameter a increases to 15.40 Å. In this case, the packing coefficient k decreases to the critical value for the condensed state (0.55). Such low values are usually observed near the isotropic transition point of mesomorphic systems. However, compound **2** undergoes the structural polymesomorphic transition in the temperature range of 140—150 °C, as evidenced by the changes in the X-ray diffraction pattern (Fig. 5, *b*). This result correlates with the DSC data (see Fig. 4) and the results of polarization microscopy (see Fig. 3).

The X-ray diffraction pattern of compound **2** measured at >165 °C (see Fig. 5, *b*) contains a series of reflections at $2\theta = 7.27$, 7.92, 8.59, 11.74, 12.56, and 13.83°. This set of reflections can be indexed in different ways, which complicates the determination of the unit cell type and, consequently, the type of ordering in the mesophase. However, taking into account the characteristic features of plastic crystals and based on the published data,[23] some conclusions can be drawn on the character of structural changes at 165 °C. The low packing coefficient characteristic of the BCC lattice immediately before the phase transition at 165 °C and the appearance of the birefringence above the polymesomorphic phase transition temperature provide convincing evidence for the hexagonal close-packed (HCP) lattice of the HT mesophase. Actually, the BCC lattice → HCP lattice transition should be accompanied by the appearance of the birefringence and an increase in the packing coefficient k. In this case, an increase in the coefficient k is a necessary condition for the existence of the HT mesophase. When considering the X-ray diffraction pattern from this point of view, the observed reflections can be indexed as 101, 003, 012, 104, 112, and 202 for the HCP lattice with the unit cell parameters $a = 15.07$ Å and $c = 33.49$ Å, the systematic absences $h + k + l = 3n$ for the HCP lattice being strictly fulfilled. In this case, the calculated packing coefficient k (0.61) can be considered as satisfactory only on the condition that the HCP unit cell contains four molecules. Evidently, another unit cell type, for example, a tetragonal or orthorhombic unit cell, can be proposed. However, a lowering of the symmetry of the unit cell with increasing temperature seems to be unlikely. Consequently, it should be assumed that the high-temperature HCP lattice points are occupied by noncovalently bonded dimers, whose stability is, apparently, determined by diphilicity of molecules **2**. Molecules **2** are characterized by the disturbed *up-and-down* symmetry, which can be favorable for this type of molecular aggregation. In addition, according to the published data,[23] two molecules with the antiprismatic arrangement of the five-membered rings can form layers with the coordination number of six. However, the absence of this segregation of molecules **2** in the LT mesophase (where this is theoretically more probable, by analogy with cyclohexasiloxanes[6,7]) remains unclear.

Therefore, using the newly synthesized compound **2** as an example, we demonstrated that molecules of cyclic siloxanes with the disturbed *up-and-down* symmetry are strongly prone to the self-organization giving rise to ordered structures. Due to the low molecular symmetry, cyclopentasiloxane **2** is a noncrystallizable compound. However, molecules **2** form a 3D mesomorphic structure (plastic crystals), which is stable throughout the temperature range below the temperature of destruction. The polymesomorphism of compound **2** is also associated with the self-organization processes resulting in the rearrangement of the location of the molecules with a low packing coefficient, without allowing the transition of the compound to the isotropic state.

A comparison of the results of the present study with the data obtained earlier[4,7] revealed the regularities of the changes in the mesomorphic properties of a series of OCS of the general formula *cis*-$[PhSi(O)(OSiMe_3)]_n$ ($n = 4$, 5, or 6). An increase in the size of the cyclic fragment of OCS has virtually no effect on thermal stability of the mesomorphic state. The high-temperature boundary of the temperature range of the existence of the mesophase is determined by the sublimation temperature of OCS. At the same time, the size of the cyclic fragment of OCS has a substantial effect on the type of ordering in the mesophase and the possibility of polymesomorphism. Thus, $\mathbf{D_4}$ forms one mesomorphic modification, *viz.*, a plastic crystal with the BCC lattice. Compound **2** ($\mathbf{D_5}$) behaves analogously to $\mathbf{D_4}$ at low temperatures and forms plastic crystals with the BCC lattice; however, compound **2** exhibits the polymesomorphic properties and forms plastic crystals with the non-cubic lattice, which is most likely the 3D hexagonal close-packed lattice, as the temperature is raised.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 04-03-321080 and 04-03-32853).

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Received November 22, 2006;
in revised form May 24, 2007