New stereoregular liquid-crystalline phenylcyclosiloxanes

N. N. Makarova,[a]★ L. M. Volkova,[a] N. V. Chizhova,[a] E. V. Matukhina,[b]
A. V. Kaznacheev,[a] and P. V. Petrovskii[a]

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 8550. E-mail: nmakar@ineos.ac.ru
[b]Department of Physics, Moscow State Pedagogical University,
1 ul. Malaya Pirogovskaya, 119882 Moscow, Russian Federation.
Fax: +7 (095) 245 0310. E-mail: lmatukh@mail.ru

Representatives of stereoregular phenylcyclotetra(hexa)siloxanes with mesogenic cyanobiphenylyl groups *cis*-oriented relatively to the siloxane ring have been synthesized for the first time. The ability of the compounds to transit to the liquid-crystalline state was confirmed by the thermooptical, X-ray diffraction, and calorimetric methods. The temperatures and enthalpies of the phase transitions were determined, and their reversibility was shown. The bilayered molecular packing with antiparallel arrangement of molecules is the most probable for the smectic A phase of the cyclosiloxanes studied. Taking into account differences in the optical textures and interlayer distances, we cannot exclude completely the possibility of formation of liquid-crystalline phases of other types.

Key words: stereoregular organocyclosiloxanes, liquid-crystalline compounds, phase transitions, hydrosilylation.

Literature data on stereoregular liquid-crystalline (LC) organosilicon compounds are lacking. The published data concern methylcyclosiloxanes, being a mixture of stereomers. This is caused by the fact that the starting methylhydridocyclosiloxanes used for the preparation of LC cyclosiloxanes are a mixture of isomers, regardless of the cycle size. For example, at least four stereomers exist for tetrahydridotetramethylcyclotetrasiloxane. Note that the number of isomers increases with an increase in the cycle size.

Liquid-crystalline methylcyclosiloxanes $[\mathrm{MeSi(Mes)O}]_n$ (Mes is mesogen, n = 4—24) have been synthesized previously,[1—5] and their properties were compared with those of the linear analogs bearing cyanobiphenylyl mesogenic groups.[1] The formation of the smectic A (SmA) phase was observed for all liquid-crystalline cyclosiloxanes. A change in the structure of the siloxane center in LC cyclic and linear polysiloxanes containing biphenylyl 4-allyloxybenzoate and cholesteryl 4-allyloxybenzoate mesogenic groups induces insignificant changes in phase transitions between them.[2] The introduction of the chiral center into the mesogenic group of LC methylcyclosiloxanes provides the ferroelectric properties and ability to spontaneous polarization in both cyclosiloxanes and their linear analogs with different degrees of polymerization.[3] The structure—property relationship for LC cyclosiloxanes and linear polymers with different lengths of the chiral terminal group and spacer was studied. The ability of LC cyclotetrasiloxanes to form the SmC* phase, which is stable in a wide interval and retains below room temperature, has been found.[4] Liquid-crystalline cyclosiloxanes with different mesogenic groups are used for the preparation of optically positive and negative materials with the rod-like structure,[5] whereas LC methylcyclotetrasiloxanes with different mesogenic groups are applied for reversible holographic recording.[6]

The purpose of this work is to synthesize stereoregular LC phenylcyclosiloxanes with *cis*-orientation of mesogenic groups relatively to the siloxane ring and to study the influence of the size of stereoregular cyclosiloxane (center of LC compounds) and the number of mesogenic groups on the phase behavior and type of packing in the LC state.

Results and Discussion

New stereoregular LC phenylcyclosiloxanes, *viz.*, the first representatives of stereoregular LC oligomers, were synthesized from *cis*-tetrahydroxy(tetraphenyl)cyclotetra- and *cis*-hexahydroxy(hexaphenyl)cyclohexasiloxanes described previously[7,8] and (4´-cyanobiphenyl-4-yl) 11-[chloro(dimethyl)silyl]undecanoate (Scheme 1, route *A*).

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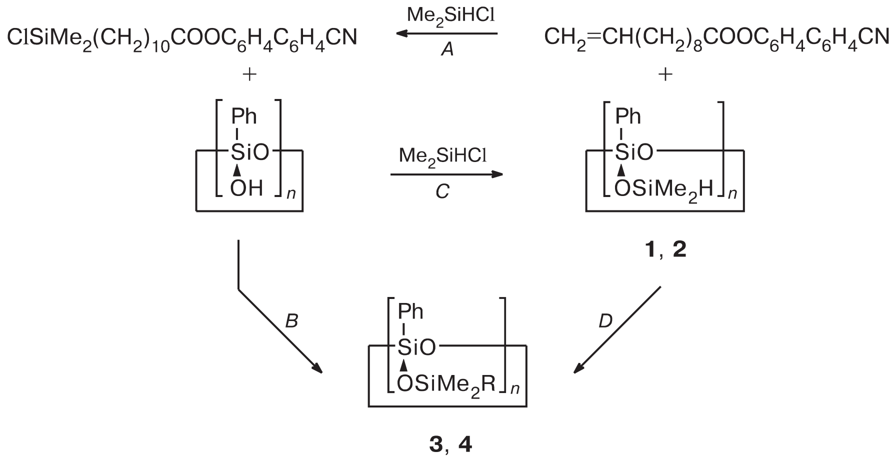
Scheme 1



n = 4 (**1**, **3**), 6 (**2**, **4**); R = $(CH_2)_{10}COOC_6H_4C_6H_4CN$

Considering the published data,[9] (4´-cyanobiphenyl-4-yl) undec-10-enoate (CBPU) used as the source of the mesogenic group makes it possible to exclude additional effects of the even-odd structure of the spacer and create an additional dipole moment.

The study of the composition of products of the reaction of *cis*-tetrahydroxy(tetraphenyl)cyclotetrasiloxane or *cis*-hexahydroxy(hexaphenyl)cyclohexasiloxane with (4´-cyanobiphenyl-4-yl) 11-[chloro(dimethyl)silyl]undecanoate (see Scheme 1, route *B*) showed that the products of incomplete substitution were present in the system along with the target product. IR spectroscopy does not always allow monitoring of the reaction products and determination of completeness of the OH group substitution, which impedes isolation and decreases the yields of compounds **3** and **4**. In order to exclude compounds with partial substitution by mesogenic groups from the composition of the reaction products, we synthesized *cis*-tetrakis(dimethylsiloxy)tetraphenylcyclotetra- (**1**) and *cis*-hexakis(dimethylsiloxy)hexaphenylcyclohexasiloxane (**2**) by the reaction of *cis*-hydroxyphenylcyclotetra(hexa)siloxanes with dimethylchlorosilane *via* route *C* (see Scheme 1). Stereoregular *cis*-phenylcyclotetra(hexa)siloxanes **3** and **4** with cyanobiphenylyl groups linked by the 10-carbon aliphatic spacer with the cyclosiloxane framework were obtained by the encounter synthesis using hydrosilylation in the reactions of compounds **1** and **2** with (4´-cyanobiphenyl-4-yl) undec-10-enoate in the presence of Karsted´s catalyst (route *D*). The reaction course was monitored using IR spectroscopy by a decrease in the intensity of the absorption band at 2138 cm^{-1} characteristic of the Si—H bond until its disappearance.

Liquid-crystalline compounds **3** and **4** synthesized *via* Scheme 1 (routes *B* and *D*) were isolated by purification from platinum using column chromatography on silica gel followed by preparative TLC. The structures of compounds **1—4** and their purity were confirmed by the data of TLC, ^1H and ^{29}Si NMR spectroscopy, IR spectroscopy, and elemental analysis.

Phase behavior. The phase behavior of compounds **3** and **4** was studied in comparison by the DSC method. The temperatures and enthalpies of the phase transitions are presented in Table 1. No differences were observed in temperatures and enthalpies of the phase transitions of compounds **3** and **4** synthesized according to routes *B* and *D*. The DSC heating and cooling curves for compounds **3** and **4** are presented in Fig. 1. Heating of the first compound results in two overlapping endothermic peaks (see Fig. 1, curve *1*). Two distinctly separated exothermic peaks at 63 and 45 °C are observed in the cooling regime (curve *2*).

For compound **4**, the heating curve contains the endothermic maximum at 45 °C and the broadened endothermic peak at 80—90 °C (see Fig. 1, curve *3*). Two exothermic peaks with maxima at 79 and 70 °C appear on cooling, and the latter is less intense and poorly resolved (see Fig. 1, curve *4*).

Table 1. Temperatures (T) and enthalpies (ΔH) of the phase transitions of phenylcyclosiloxanes **3** and **4**

Com-pound	T_v/°C	T_{Cr-SmA} /°C	ΔH_{Cr-SmA} /J g^{-1}	T_{SmA-I} /°C	ΔH_{SmA-I} /J g^{-1}
3	−4.0	55.0	4.5	66.0	11.5
4	−1.0	50.0	9.4	84.5	11.0

Note. Cr is crystal, SmA is smectic A phase, and I is isotropic melt; T_v is the vitrifying temperature.

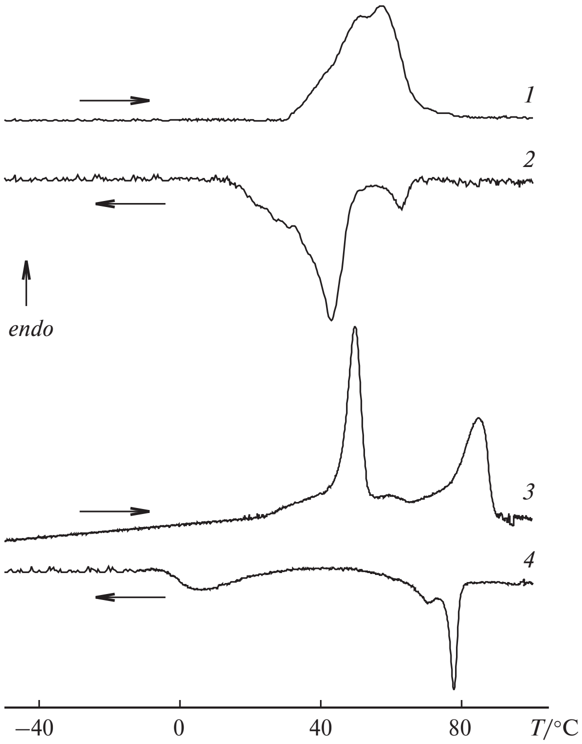


Fig. 1. DSC data for compounds **3** (*1*, *2*) and **4** (*3*, *4*): heating (*1*, *3*) and cooling (*2*, *4*) curves. The rate of heating and cooling is 10 °C min^{-1}.

For considered compounds **3** and **4**, the vitrifying temperatures (T_v) differ insignificantly and agree with the previously published values for LC methylcyclosiloxanes with different mesogens, which are a mixture of stereoisomers with different numbers of the SiO siloxane fragments (n = 4—7).[5] As previously established for the isotropization temperature (T_i), it does not unambiguously depend on the cyclosiloxane size, mesogen structure, or spacer length. For LC methylcyclosiloxanes with cholesteryl groups, T_i increases with an increase in the cyclosiloxane size or an elongation of the spacer for mesogens of the aromatic ester type.[5] We found that T_i increased with an increase in the size of cyclosiloxanes, *i.e.*, an increase in the number of mesogenic groups *cis*-oriented relatively to the cyclosiloxane plane enhances intermolecular interactions and stabilizes the LC state.

The isotropization enthalpies (ΔH_i) for compounds **3** and **4** are close to analogous characteristics published for siloxane polymers with the lateral alkoxycyanobiphenylyl groups and alkyl 11-carbon spacer (ΔH_i = 9.2 J g^{-1}), which form the SmA phase with parallel packing of regions of the main chains.[10]

It is established by polarization optical microscopy that compounds **3** and **4** are crystalline at 20 °C. With temperature increasing, they first transit to the LC state and are isotropized at 78.0 and 83.0 °C, respectively. Anisotropic drops are initiated on cooling of compound **3** from the isotropic melt at 77.5 °C (Fig. 2, *a*). The further cooling to 62.0 °C with a rate of 0.5 °C min^{-1} shows the growth of primary formations with a point defect in the drop center (Fig. 2, *b*). It is seen from the data in Fig. 2, *a*, *b* that the anisotropic and isotropic phases coexist in the temperature interval of ~15 °C. The resulting texture in the form of drops resembles textures corresponding to the nematic and smectic (SmA) phases.[11] However, similar textures were observed for several LC compounds with different structures of the center forming the different LC phases: for the hexahydro-1,3,5-triazine derivatives forming the columnar phase,[12] the trisubstituted 1,4,7-triazacyclononane metal complex with carbonyl groups (columnar phase of the pyramid-like type),[13] and discotic compounds with the tricycloquinazoline cycle.[14] The texture formation is completed at 18 °C. However, no changes related to crystallization are observed immediately after cooling (Fig. 2, *c*). The coexistence of the LC and crystalline phases was detected after 2 days (Fig. 2, *d*). The crystal structure is recovered completely after 5 days (Fig. 2, *e*). On cooling of an isotropic melt of compound **4**, unlike compound **3**, LC nuclei are formed as sticks at 75 °C (Fig. 3, *a*). The isotropic space is filled with the SmA smectic phase in the 75—55 °C interval (Fig. 3, *b—d*). The coexistence of the isotropic and anisotropic phases is detected in a wide temperature interval.

According to the X-ray diffraction data, compounds **3** and **4** at 20 °C are crystalline (Figs. 4 and 5, curves *1*). The X-ray diffraction method failed to detect the transition of these compounds to the LC state on heating because of close temperatures of transition to the LC state and isotropization, which were determined by DSC and polarization microscopy. The diffraction pattern of compound **3** obtained at 65 °C indicates its transition to the melt: it contains two amorphous halos at 2θ = 8.19 (d_{a1} = 10.78 Å, $\Delta_{1/2}$ = 2.5°) and 18.69° (d_{a2} = 4.80 Å, $\Delta_{1/2}$ = 4.5°) (see Fig. 4, curve *2*).

Consideration of the diffraction patterns of compound **4** obtained at 20 °C and during heating at temperatures above 45 °C (see Fig. 5, curves *1* and *2*) shows that the endothermic effect in the DSC curve at 43 °C (see Fig. 1, curve *3*) is related to the crystal—crystal transition. The 80—90 °C region exhibits only the crystal—melt transition: the diffraction pattern at 85 °C (see Fig. 5, curve *3*) contains two amorphous reflections at $2\theta_{a1}$ = 6.99 (d_{a1} = 12.63 Å, $\Delta_{1/2}$ = 1.74°) and 19.94° (d_{a2} = 4.45 Å, $\Delta_{1/2}$ = 5.7°).

According to the X-ray diffraction data, no crystallization is observed on cooling compounds **3** and **4** from temperatures at which they are in the isotropic state to 20 °C (see Fig. 4, curve *3* and Fig. 5, curve *4*) but both compounds form the smectic phase. A narrow low-inten-

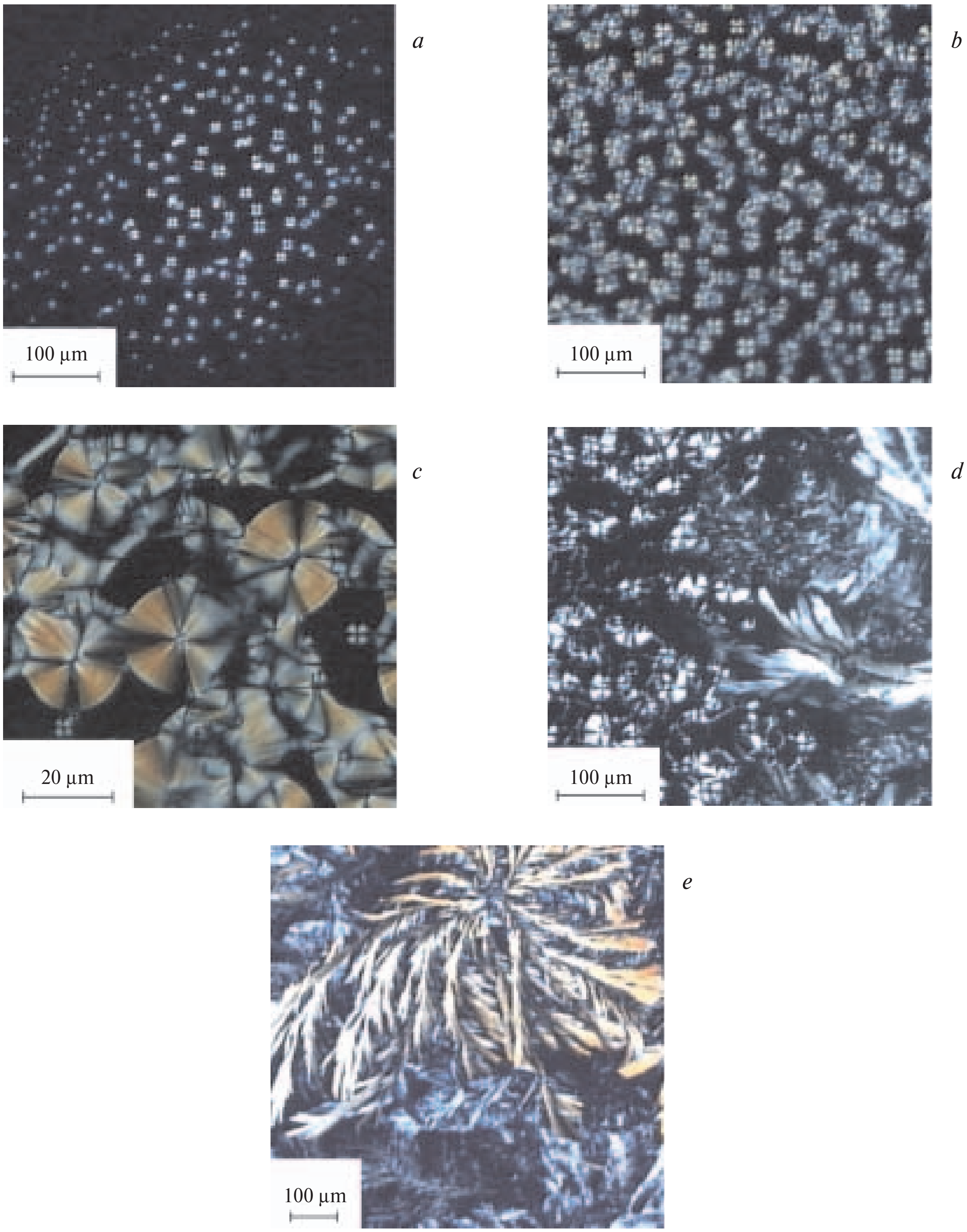


Fig. 2*. Optical microphotographs of the textures of compound **3** (cooling rate 0.5 °C $\min^{-1}$ from 80 °C): at 77.5 (*a*), 62.0 (*b*), 18.0 (*c*), 15 °C after 2 days (*d*), and 17.0 °C after 5 days (*e*).

sity reflection appears at 2θ* in the diffraction pattern of cyclosiloxanes **3** and **4**, and two amorphous halos characteristic of the melt are retained. The angular position of the reflection of the mesophase is $2\theta^* = 3.48$ ($d^* = 25.53$ Å, $\Delta_{1/2} = 0.30°$) and 3.32° ($d^* = 26.58$ Å, $\Delta_{1/2} = 0.30°$) for compounds **3** and **4**, respectively. Note that for both

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* Figure 2 is available in full color in the on-line version of the journal (http://www.wkap.nl/journalhome.htm/1066-5285) and on the web site of the journal (http://rcb.ioc.ac.ru).

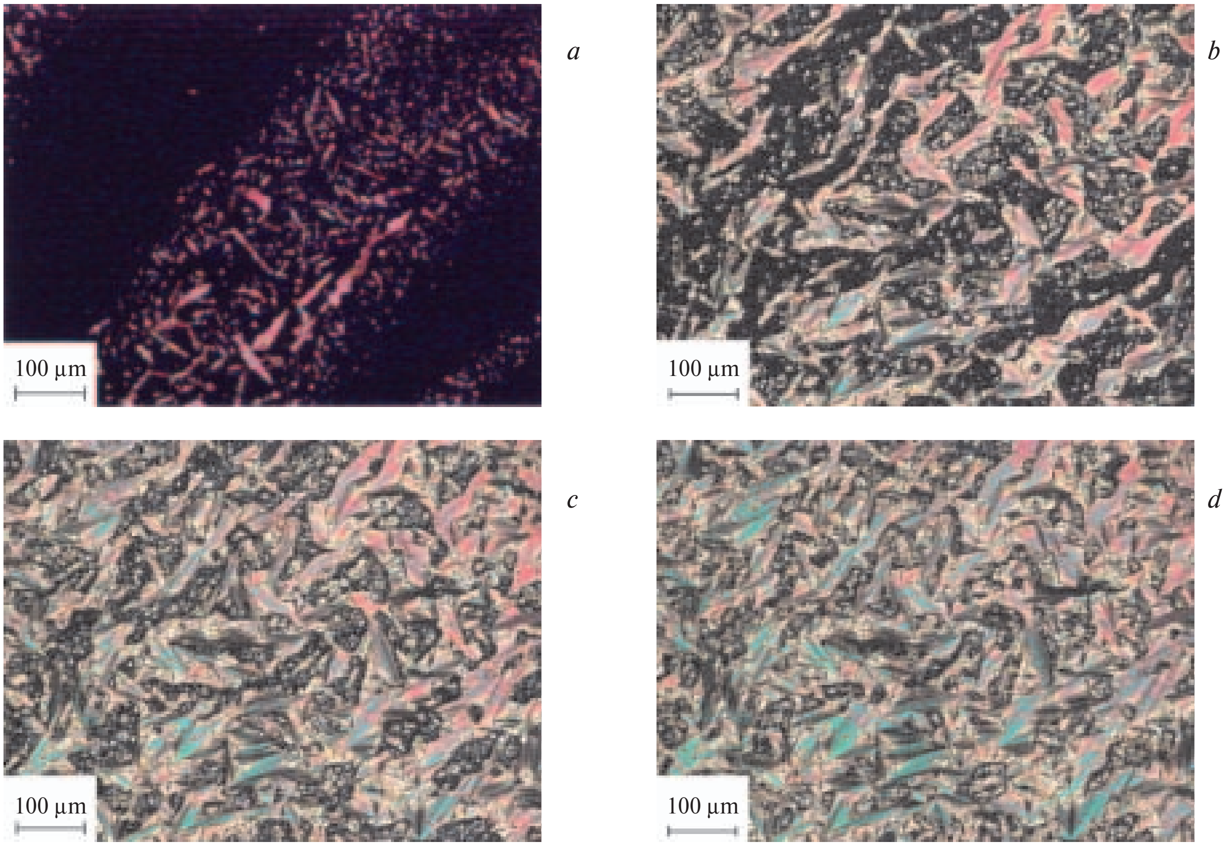

Fig. 3*. Optical microphotographs of the textures of compound **4** (cooling rate 0.5 °C min^{-1} from 80 °C): at 75 °C (*a*), at 65 °C and storage for 20 min in the isothermic regime (*b*), at 55 °C and storage for 20 min in the isothermic regime (*c*), and 45 °C (*d*).

cyclosiloxanes the position of the maximum of the first amorphous halo ($2\theta_{a1}$) is displaced substantially toward larger angles with the temperature decrease. An analogous characteristic of the second halo ($2\theta_{a2}$) changes insignificantly. For example, at 20 °C for compound **3** $2\theta_{a1} = 8.47°$ ($d_{a1} = 10.43$ Å), $2\theta_{a2} = 18.84°$ ($d_{a2} = 4.80$ Å), and for compound **4** $2\theta_{a1} = 7.30°$ ($d_{a1} = 12.10$ Å), $2\theta_{a2} = 19.81°$ ($d_{a2} = 4.48$ Å). The different sensitivities of the $2\theta_{a1}$ and $2\theta_{a2}$ parameters to temperature changes indicates that the $2\theta_{a1}$ and $2\theta_{a2}$ amorphous maxima are responsible for scattering on different molecular fragments.

It should be mentioned that the $2\theta_{a2}$ value for compounds **3** and **4** almost coincides with the angular position of the maximum of the single amorphous halo, which is present in the diffraction pattern of the mesogen in the SmA phase and for which $2\theta_a = 4.67°$. Therefore, the amorphous maxima at $2\theta_{a2}$ observed in the diffraction patterns of compounds **3** and **4** are mainly responsible for scattering on the mesogenic groups. The calculated d_{a2} values for compounds **3** and **4** somewhat differ ($d_{a2} = 4.80$ and 4.45 Å, respectively), *i.e.*, a change in the type of the siloxane cycle affects the statistics of the intra- and intermolecular distances for the mesogenic groups. In particular, the more compact packing of the latter observed for the mesophase of compound **4** can be one of the factors favoring an increase in its thermal stability.

The above presented d_{a1} values calculated for compounds **3** and **4** are close to the thicknesses of the tetra- and hexasiloxane cyclic fragments with the lateral phenyl groups. This fact and the high gradient of the $2\theta_{a1}(T)$ dependence suggest that the first amorphous halo at $2\theta_{a1}$ is mainly responsible for intermolecular scattering on the cyclic fragments. Therefore, the short-range order of arrangement of cyclic fragments exists in the layer, and the most strict correlation is observed in the direction perpendicular to the plane of the cycles. In this connection, we can assert that microphase separation occurs in the mesophase between the mesogenic groups and siloxane cycles, which is also retained upon transition to the isotropic melt.

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* Figure 3 is available in full color in the on-line version of the journal (http://www.wkap.nl/journalhome.htm/1066-5285) and on the web site of the journal (http://rcb.ioc.ac.ru).

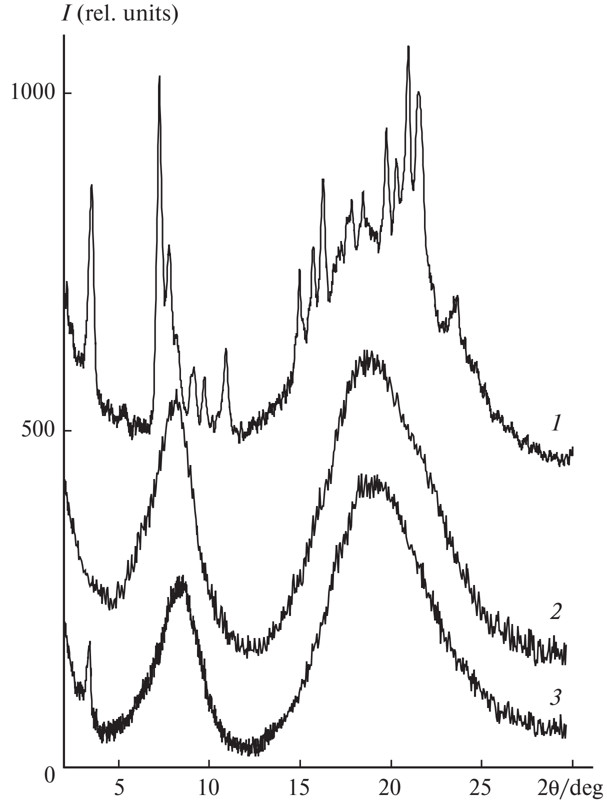

Fig. 4. Diffraction patterns of compound **3** at 20 (*1*), 65 (*2*), and 20 °C after cooling from 80 °C (*3*). The diffraction pattern of the sample obtained on cooling from 80 to 20 °C and stored for 2 days coincides with the diffraction pattern of the starting sample (curve *1*).

The results obtained give the following sequence of phase transformations for compounds **3** and **4** on heating (*) and cooling (**).

Mesogen CBPU

$$\mathrm{Cr} \overset{50\ ^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{SmA} \overset{67\ ^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{I}$$

Compound **3**

$$\mathrm{Cr^{*}} \xrightarrow{58\ ^\circ\mathrm{C}} \mathrm{SmA} \xrightarrow{78\ ^\circ\mathrm{C}} \mathrm{I}$$

$$\mathrm{SmA^{**}} \xleftarrow{62\ ^\circ\mathrm{C}} \mathrm{I}$$

Compound **4**

$$\mathrm{Cr^{*}} \xrightarrow{43\ ^\circ\mathrm{C}} \mathrm{Cr} \xrightarrow{83\ ^\circ\mathrm{C}} \mathrm{SmA} \xrightarrow{86\ ^\circ\mathrm{C}} \mathrm{I}$$

$$\mathrm{SmA^{**}} \xleftarrow{79\ ^\circ\mathrm{C}} \mathrm{I}$$

Cr is crystal, I is isotropic melt

Comparing the data obtained for the mesogen CBPU and compounds **3** and **4**, one can conclude the following: LC stereoregular cyclosiloxanes are characterized by the higher thermal stability of the crystalline and LC phases compared to the starting mesogenic compound. The temperature region of existence of the SmA phase of cyclosiloxanes in the heating regime decreases due to a more considerable increase in T_m compared to T_i. At the same time, the low crystallization rate inherent in compounds **3** and **4** makes it possible to enlarge significantly the temperature region of existence of the SmA phase in the regime of cooling from melt. An increase in the number of mesogenic groups on going from the tetra- to hexasiloxane cycle results in the appearance of the polymorphic properties and an increase in the melting and isotropization temperatures.

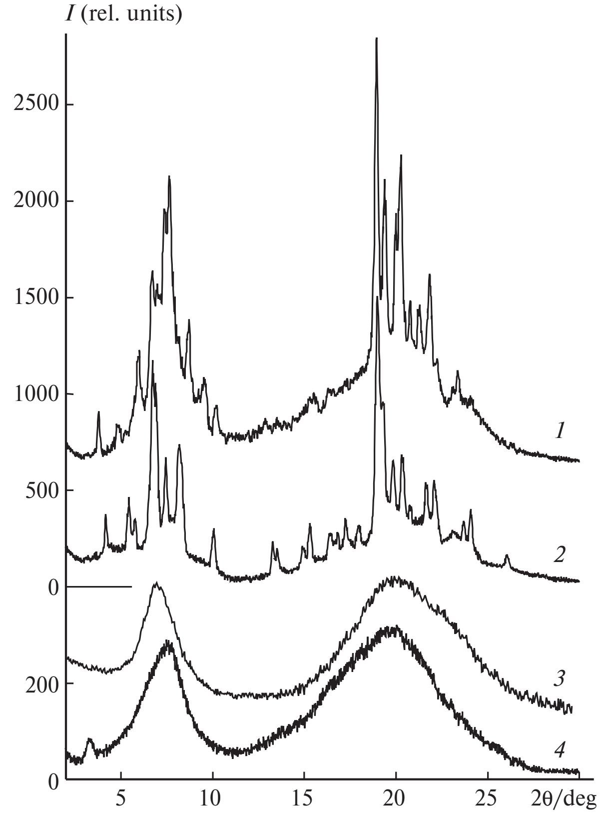

Fig. 5. Diffraction patterns of compound **4** at 20 (*1*), 50 (*2*), 85 (*3*), and 20 °C after cooling from 85 °C (*4*).

The values found for the interplanar distances d^* (25.53 and 26.61 Å for compounds **3** and **4**, respectively) are much lower than the interlayer periodicity for the monomolecular layered packing calculated from the known values for the mesogenic group length (L = 27.9 Å)[★] and thicknesses of cyclosiloxanes with the phenyl substituents ($L^* \approx$ 10—12 Å). Taking into account all specific features listed above for the diffraction patterns of the compounds under study in the mesophase, we can assert that the most probable model of their molecular packing in the SmA

[★] The L value was obtained by the HyperChem 4.5 program on a Silicon Graphics computer.

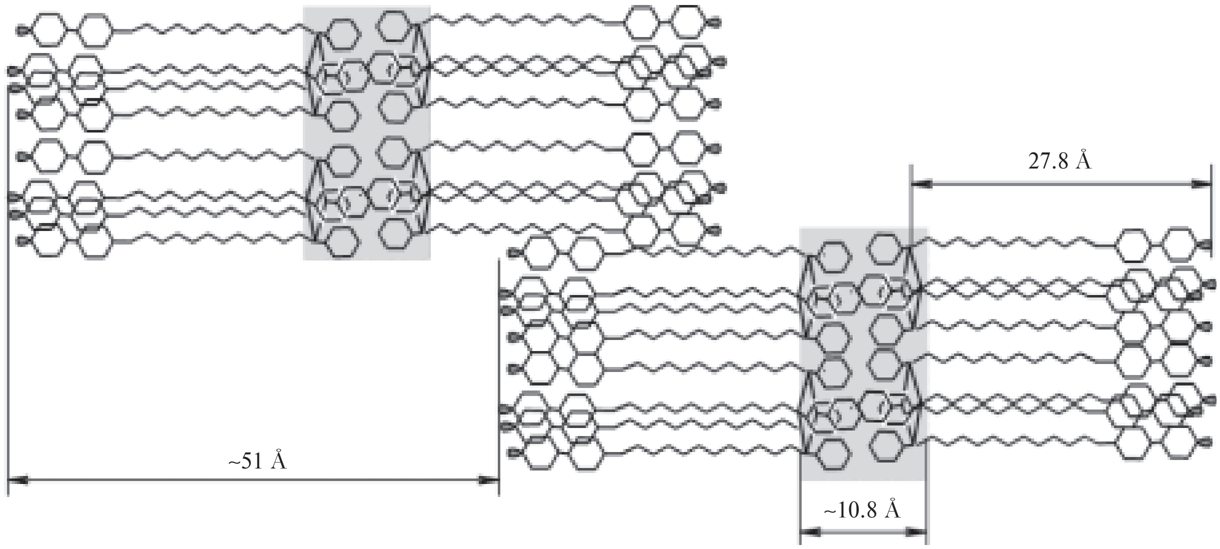

Fig. 6. Scheme of molecular packing in the SmA phase for compounds **3** and **4**. The layers are vertical. The region of the increased electron density is emphasized.

phase is the bilayered antiparallel packing of molecules (Fig. 6) in which the interlayer periodicity is $d = 2d^* = 51.0$ and 53.2 Å for compounds **3** and **4**, respectively. Segregation of the siloxane cycles increases the electron density in the center of the layer, which results in damping of reflection 001 (direction <00l> coincides with the normal to the plane of the layer), and index 002 should be ascribed to the reflection detected at $2\theta^*$. The model proposed is characterized by a sufficiently strong overlap of the mesogenic groups at the interlayer level. This is experimentally confirmed by the low d_{a2} values.

It should be mentioned in conclusion that the textures obtained for compounds **3** and **4** differ significantly. This can be related to several factors, in particular, to different packing of the cyclic nuclei in the center of the layer. This assumption is favored by substantial differences in the d^* and d_{a1} values for compounds **3** and **4** caused, most probably, by the thickness of the tetra- and hexasiloxane cycles with the phenyl substituents. At the same time, an influence of other factors and the possibility of alternative variants of molecular packing cannot be excluded. For example, the different packing models have previously been proposed for other LC organocyclosiloxanes: discotic and sheaf-like[5] (with the uniform distribution of the mesogenic groups from the cycle plane). The structures of the LC phases of the compounds under study will be refined for the macroscopically oriented samples.

Experimental

^1H and ^{29}Si NMR spectra were recorded on a Bruker AMX-400 spectrometer at 20 °C in a $CDCl_3$—CCl_4 (~1 : 1) mixture. IR spectra were obtained on a Specord M-82 spectrometer (KBr pellets). Temperatures and enthalpies of phase transitions were determined by the DSC method on a Perkin—Elmer DSC-7 instrument (heating rate 10 °C min^{-1}). X-ray diffraction studies were carried out on a Dron-3M diffractometer. Before measurements, the temperature of samples was maintained constant for 20 min within ±1 °C. The phase state of samples was determined by optical polarization microscopy on an Axiolab Pol microscope (Zeiss) equipped with a heating stage with a controling system (Linkam). Compounds **3** and **4** were separated by preparative TLC on Silufol plates (20×20 cm) in a glass chamber with a glass ground cover 18.0×7.0×17.0 cm in size. Two spots were observed on plates upon UV irradiation. Each substance was extracted with Et_2O and toluene. The structures of the compounds were established on the basis of the data of ^1H and ^{29}Si NMR spectroscopy, IR spectroscopy, and elemental analysis.

(4´-Cyanobiphenyl-4-yl) undec-10-enoate was synthesized using a known procedure[12] by the acylation of 4´-cyanobiphenyl-4-ol with undec-10-enoyl chloride in anhydrous THF in the presence of Et_3N. The yield was 80% after double recrystallization from EtOH, m.p. 49.5 °C, $T_{N-I} = 75.0$ °C.

cis-Tetrahydroxy(tetraphenyl)cyclotetrasiloxane was synthesized according to a published procedure,[7] m.p. 184—186 °C. ^{29}Si NMR (acetone-d_6), δ: –69.79 (s).

***cis*-Tetrakis(dimethylsiloxy)tetraphenylcyclotetrasiloxane (1).** Me_2SiHCl (1.50 g, 15.5 mmol) in Et_2O (10 mL) was placed in a three-necked flask equipped with a thermometer, reflux condenser, a dropping funnel, and a magnetic stirrer. *cis*-Tetrahydroxy(tetraphenyl)cyclotetrasiloxane (0.92 g, 2.17 mmol) and Py (1.02 g, 12.0 mmol) in absolute Et_2O (40 mL) were added from a dropping funnel. The mixture was stirred for 3 h at 20 °C and for 5 h at 34 °C. The IR spectrum contained no absorption band characteristic of the Si—OH bond (3400—3700 cm^{-1}). The precipitate was filtered off, Et_2O was distilled off, and compound **1** (0.80 g, 61.0%) was obtained by fractional distillation, b.p. 175—180 °C ($6 \cdot 10^{-3}$ Torr). Found (%): C, 48.78; H, 6.11; Si, 28.48. $C_{32}H_{48}O_8Si_8$. Calculated (%): C, 48.93; H, 6.17; Si, 28.60. IR, ν/cm^{-1}: 808, 846 ($SiMe_2$); 909 (Si—Me); 1068

(SiOSi); 1136 (Si—Ph); 1260 (Si—Me); 1430 (Ph—Si); 2143 (Si—H); 2964 (Me); 3050, 3070 (Ph). ^{1}H NMR, δ: 0.32 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 4.91 (sept, 1 H, $\underline{H}(CH_3)_2SiO$, ^3J = 2.8 Hz); 7.13 (t, 2 H, *m*-CH, ^3J = 8.0 Hz); 7.29 (t, 1 H, *p*-CH, ^3J = 8.0 Hz); 7.33 (d, 2 H, *o*-CH, ^3J = 8.0 Hz). ^{29}Si NMR, δ: −3.92 (s, 2 Si, $H(CH_3)_2SiO$); −3.96 (s, 2 Si, $H(CH_3)_2SiO$); −78.35 (s, $PhSiO_{3/2}$).

***cis*-Hexakis(dimethylsiloxy)hexaphenylcyclohexasiloxane (2).** Me_2SiHCl (0.61 g, 6.5 mmol) in absolute Et_2O (5 mL) was placed in a three-necked flask equipped with a thermometer, a reflux condenser, a dropping funnel, and a magnetic stirrer. *cis*-Hexahydroxy(hexaphenyl)cyclohexasiloxane**[8]** (0.43 g, 0.52 mmol) and Py (0.36 g, 4.5 mmol) in absolute Et_2O (19 mL) and DMAP (0.002 g) were added from a dropping funnel for 30 min. The mixture was stirred for 3 h at 20 °C and for 5 h at 34 °C. The reaction course was monitored by IR spectroscopy from the disappearance of the absorption band characteristic of the Si—OH bond at 3400—3700 cm^{-1}. After 2 days, absorption bands of the Si—OH bond were absent from the IR spectrum. The precipitate was filtered off, and Et_2O was distilled off. An excess of Me_2SiHCl was removed *in vacuo*. Compound **2** was obtained (0.55 g, 91.5%), R_f 0.67 (heptane—toluene, 1 : 9), T_i = 245—248 °C. Found (%): C, 48.80; H, 6.20; Si, 28.77. $C_{48}H_{72}O_{12}Si_{12}$. Calculated (%): C, 48.93; H, 6.17; Si, 28.60. IR, ν/cm^{-1}: 761, 860 ($SiMe_2$); 897 (Si—Me); 1063 (Si—O); 1131 (Si—Ph); 1242 (Si—Me); 1390, 1468 (Me, CH_2); 2132 (Si—H); 2953 (Me); 3045, 3060 (Ph). ^{1}H NMR, δ: 0.25 (d, 6 H, $H(C\underline{H}_3)_2SiO$, ^3J = 2.8 Hz); 4.87 (sept, 1 H, $\underline{H}(CH_3)_2SiO$, ^3J = 2.8 Hz); 6.95 (t, 2 H, *m*-CH, ^3J = 7.2 Hz); 7.17 (d, 2 H, *o*-CH, ^3J = 7.2 Hz); 7.21 (t, 1 H, *p*-CH, ^3J = 7.2 Hz). ^{29}Si NMR, δ: −4.46 (s, 2 Si, $H(CH_3)_2SiO$); −3.96 (s, 2 Si, $H(CH_3)_2SiO$); −80.27 (s, $PhSiO_{3/2}$).

***cis*-Tetrakis{[(4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethyl)siloxy}(tetraphenyl)cyclotetrasiloxane (3).** *A* (route *B*, see Scheme 1). (4´-Cyanobiphenyl-4-yl) 11-[chloro(dimethyl)silyl]undecanoate (0.31 g, 0.68 mmol) in Et_2O (5 mL) was placed in a three-necked flask filled with argon and equipped with a reflux condenser, a thermometer, and a magnetic stirrer. *cis*-Tetrahydroxy(tetraphenyl)cyclotetrasiloxane (0.046 g, 0.083 mmol) and Et_3N (0.06 mL) in toluene (4 mL) were added with stirring. The reaction mixture was stirred for 6 h at 20 °C and for 15 h at 100 °C. The precipitate formed was separated, the reaction mixture was washed with water, the organic layer was dried over $CaCl_2$, and the solvent was distilled off. The reaction products were separated by preparative TLC using a toluene—heptane—AcOEt (1.0 : 0.2 : 0.1) mixture as eluent; for compound **3** R_f 0.38, upon repeated elution R_f 0.54. The products from plates were extracted with Et_2O. Compound **3** was obtained in 56.0% yield (0.10 g). Found (%): C, 68.48; H, 7.04; N, 2.23, Si, 10.30. $C_{128}H_{156}N_4O_{16}Si_8$. Calculated (%): C, 68.90; H, 7.04; N, 2.51; Si, 10.07. IR, ν/cm^{-1}: 791, 842 ($SiMe_2$); 915 (Si—Me); 1062 (SiOSi); 1136 (Si—Ph); 1170 ($CO(CH_2)$); 1255 (Si—Me); 1379, 1430 (Ph—Si); 1492, 1611 (C_6H_4); 1758 (C=O); 2234 (C≡N); 2857, 2925 (CH_2); 3020, 3050, 3072 (Ph, C_6H_4). ^{1}H NMR, δ: 0.17 (s, 6 H, $(C\underline{H}_3)_2SiO$); 0.52 (m, 2 H, CH_2SiO); 1.39 (quint, 2 H, $CH_2—C\underline{H}_2—CH_2$, ^3J = 7.6 Hz); 1.41 (m, 6 H, $CH_2—C\underline{H}_2—CH_2$); 1.76 (quint, 2 H $C(O)—CH_2—C\underline{H}_2$, J = 7.6 Hz); 2.55 (t, 2 H, $C(O)—C\underline{H}_2$, ^3J = 7.6 Hz); 7.04 (t, 2 H, *m*-CH, ^3J = 7.6 Hz); 7.16 (t, 1 H, *p*-CH, J = 7.2 Hz); 7.16 (d, 2 H, CH—C—CN, ^3J = 8.8 Hz); 7.24 (d, 2 H, *o*-CH, ^3J = 7.6 Hz); 7.55 (d, 2 H, $C\underline{H}$—CH—C—N, C_6H_4CN, ^3J = 8.8 Hz); 7.62 (d, 2 H, $C\underline{H}$—CH—C—O, ^3J = 8.4 Hz); 7.70 (d, 2 H, CH—$C\underline{H}$—C—O, C_6H_4O, ^3J = 8.4 Hz). ^{29}Si NMR, δ: 10.72 (s, $CH_2(CH_3)_2SiO$); −79.62 (s, $PhSiO_{3/2}$).

B (route *D*, see Scheme 1). Compound **1** (0.10 g, 0.12 mmol) and (4´-cyanobiphenyl-4-yl) undec-10-enoate (0.18 g, 0.51 mmol) in toluene (0.6 mL) were placed in a three-necked flask filled with argon and equipped with a reflux condenser, a thermometer, and a magnetic stirrer. Karsted´s catalyst (Aldrich, PC072) (5 μL or recalculated [Pt] = $1.56 \cdot 10^{-6}$ mol L^{-1}) was added with stirring. The reaction mixture was heated for 2 h at 50 °C. The reaction course was monitored by IR spectroscopy from the disappearance of the absorption band characteristic of the Si—H bond at 2138 cm^{-1}. Compound **3** was obtained in 49.5% yield (0.11 g) by preparative TLC using a toluene—hexane—AcOEt (1.0 : 0.2 : 0.1) mixture as an eluent, R_f 0.34 (for repeated elution, R_f 0.52), T_i 67—70 °C. Found (%): C, 68.73; H, 7.14; N, 2.37, Si, 10.08. $C_{128}H_{156}N_4O_{16}Si_8$. Calculated (%): C, 68.90; H, 7.04; N, 2.51; Si, 10.07. IR, ν/cm^{-1}: 791, 842 ($SiMe_2$); 897 (Si—Me); 1063 (SiOSi); 1131 (Si—Ph); 1178 ($CO(CH_2)$); 1242 (Si—Me); 1430 (PhSi); 1492, 1611 (C_6H_4); 1758 (C=O); 2234 (C≡N); 2857, 2925 (CH_2); 3025, 3056, 3072 (Ph, C_6H_4). ^{1}H NMR, δ: 0.17 (s, 6 H, $(C\underline{H}_3)_2SiO$); 0.59 (m, 2 H, CH_2SiO); 1.23 (m, 6 H, $CH_2—C\underline{H}_2—CH_2$, J = 7.6 Hz); 1.32 (quint, 2 H, $CH_2—C\underline{H}_2—CH_2$, ^3J = 7.6 Hz); 1.75 (quint, 2 H, $C(O)—CH_2—C\underline{H}_2$, J = 7.6 Hz); 2.56 (t, 2 H, $C(O)—C\underline{H}_2$, ^3J = 7.6 Hz); 7.05 (t, 2 H, *m*-CH, ^3J = 7.6 Hz); 7.17 (d, 2 H, CH—C—CN, ^3J = 7.2 Hz); 7.22 (t, 1 H, *p*-CH, ^3J = 7.2 Hz); 7.25 (d, 2 H, *o*-CH, ^3J = 7.6 Hz); 7.56 (d, 2 H, $C\underline{H}$—CH—C—N, C_6H_4CN, ^3J = 7.2 Hz); 7.63 (d, 2 H, $C\underline{H}$—CH—C—O, ^3J = 8.0 Hz); 7.70 (d, 2 H, CH—$C\underline{H}$—C—O, C_6H_4O, ^3J = 8.0 Hz). ^{29}Si NMR, δ: 10.73 (s, $CH_2(CH_3)_2SiO$); −79.70 (s, $PhSiO_{3/2}$).

***cis*-Hexakis{[(4´-cyanobiphenyl-4-yloxycarbonyl)dec-10-yl](dimethyl)siloxy}(hexaphenyl)cyclohexasiloxane (4).** Compound **2** (0.42 g, 0.36 mmol) and (4´-cyanobiphenyl-4-yl) undec-10-enoate (0.94 g, 2.60 mmol) in toluene (2.7 mL) were placed in a three-necked flask filled with argon equipped with a reflux condenser, a thermometer, and a magnetic stirrer. Karsted´s catalyst (5 μL, recalculated [Pt] = $1.56 \cdot 10^{-6}$ mol L^{-1}). The reaction mixture was heated for 5 h at 65 °C. The absorption band at 2138 cm^{-1} characteristic of the Si—H bond was absent from the IR spectrum. Compound **4** was obtained in 41.5% yield (0.50 g) by preparative TLC using a toluene—hexane—AcOEt mixture (1.00 : 0.23 : 0.11) as eluent, R_f 0.27, T_i 83—85 °C. Found (%): C, 68.73; H, 7.14; N, 2.37; Si, 10.08. $C_{192}H_{234}N_6O_{24}Si_{12}$. Calculated (%): C, 68.89; H, 7.04; N, 2.51; Si, 10.07. IR, ν/cm^{-1}: 790, 842 ($SiMe_2$); 897 (Si—Me); 1068 (SiOSi); 1136 (Si—Ph); 1178 ($CO(CH_2)$); 1255 (Si—Me); 1460 (Me, CH_2); 1492, 1611 (C_6H_4); 1758 (C=O); 2234 (C≡N); 2857, 2925 (CH_2); 3050, 3070 (Ph). ^{1}H NMR, δ: 0.16 (s, 6 H, $(CH_3)_2SiO$); 0.56 (m, 2 H, CH_2SiO); 1.20 (m, 14 H, $CH_2—C\underline{H}_2—CH_2$, J = 7.6 Hz); 1.39 (quint, 2 H, $CH_2—C\underline{H}_2—CH_2$); 1.74 (quint, 2 H, $C(O)—CH_2—C\underline{H}_2$, ^3J = 7.6 Hz); 2.55 (t, 2 H, $C(O)CH_2$, ^3J = 7.6 Hz); 6.86 (t, 2 H, *m*-CH, ^3J = 7.6 Hz); 7.10 (t, 1 H, *p*-CH, ^3J = 7.2 Hz); 7.16 (d, 2 H, CH—C—CN, ^3J = 7.2 Hz); 7.16 (d, 2 H, *o*-CH, ^3J = 7.2 Hz); 7.53 (d, 2 H, $C\underline{H}$—CH—C—N, C_6H_4CN, ^3J = 7.2 Hz); 7.61 (d, 2 H, $C\underline{H}$—CH—C—O, ^3J = 8.0 Hz); 7.67 (d, 2 H, CH—$C\underline{H}$—C—O, C_6H_4O, ^3J = 8.0 Hz). ^{29}Si NMR, δ: 9.88 (s, $CH_2(CH_3)_2SiO$); −83.43 (s, $PhSiO_{3/2}$).

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