

## *cis*-Tetra[(organo)(trimethylsiloxy)]cyclotetrasiloxanes: synthesis and mesomorphic properties

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Hydrolytic condensation of organotrialkoxysilanes  $\text{RSi}(\text{OR}')_3$  ( $\text{R} = \text{Me, Et, Pr, CH}=\text{CH}_2$ ;  $\text{R}' = \text{OMe, OEt}$ ) in the presence of sodium and/or potassium hydroxide gave new alkali organosiloxanates  $\{(\text{M}^+)_4[\text{RSi}(\text{O})\text{O}^-]_4\} \cdot n\text{L}$  ( $\text{R} = \text{Me, Et, Pr, CH}=\text{CH}_2$ ;  $\text{M} = \text{Na, K}$ ;  $\text{L} = \text{R}'\text{OH, H}_2\text{O}$ ) in which the main structural fragment is the cyclotetrasiloxanolate fragment *cis*- $[\text{RSi}(\text{O})\text{O}^-]_4$ . Based on these organosiloxanates, a series of *cis*-tetra[(organo)(trimethylsiloxy)]cyclotetrasiloxanes was synthesized. For new cyclotetrasiloxanes, the thermotropic transitions and mesomorphic orderings were determined by differential scanning calorimetry, X-ray diffraction analysis, and polarization microscopy. In addition, new mesomorphic compounds were revealed. The character of thermotropic and time evolution of the phase state was found for a mixture of *cis*-tetra[ethyl(trimethylsiloxy)]- and *cis*-tetra[phenyl(trimethylsiloxy)]cyclotetrasiloxanes.

**Key words:** hydrolytic condensation, organotrialkoxysilanes, alkali organosiloxanates, stereoregular organocyclosiloxanes, trimethylsilylation, mesomorphic state, phase transitions, plastic crystals, differential scanning calorimetry, X-ray diffraction analysis, polarization microscopy.

Processes of self-organization of molecules into mesomorphic structures having no mesogenic groups produce two types of non-crystalline ordered systems: 3D- and 2D-columnar (condis\* type) and 3D-ordered plastic crystals (odis\* type). The formation of various columnar structures is characteristic of many polymeric compounds, including polyorganosiloxanes. At the same time, the ability of monomeric organosiloxanes to form non-crystalline ordered structures is still not understood.

In the series of symmetrically substituted organocyclotetrasiloxanes only one mesomorphic compound is known.<sup>1</sup> This is octaphenylcyclotetrasiloxane (OPhCTS) that forms the plastic-crystalline mesophase (odis phase) in a narrow temperature range. When the Ph groups at the Si atoms are substituted for aliphatic groups, cyclotetrasiloxane loses its capability of mesomorphic ordering. Octamethylcyclotetrasiloxane (OMeCTS), octaethylcyclotetrasiloxane (OEtCTS), and octapropylcyclotetrasiloxane (OPrCTS) undergo crystal  $\rightarrow$  melt transitions omitting the stage of mesomorphic state.<sup>2</sup>

\* Condis means "conformationally disordered," and odis is "orientationally disordered."

We have shown previously<sup>3</sup> that the replacement of some Ph groups in OPhCTS by the  $\text{Me}_3\text{SiO}$  groups extends substantially the temperature interval where the odis phase exists (Table 1). Thus, the broken "up-and-down" symmetry inherent in the molecules of *cis*-tetra[(phenyl)(trimethylsiloxy)]cyclotetrasiloxane *cis*- $[\text{PhSi}(\text{O})\text{OSiMe}_3]_4$  ( $\text{D}_4\text{Ph}$ ) does not suppress the ability to transition to the mesomorphic state and, moreover, enhances substantially its thermal stability.

Therefore, in the present work we studied a series of cyclotetrasiloxanes with the broken "up-and-down" symmetry in which the Ph groups are substituted for the aliphatic (Me, Et, and Pr) and vinyl groups: *cis*- $[\text{RSi}(\text{O})\text{OSiMe}_3]_4$  with  $\text{R} = \text{Me}$  ( $\text{D}_4\text{Me}$ ),  $\text{Et}$  ( $\text{D}_4\text{Et}$ ),  $\text{Pr}$  ( $\text{D}_4\text{Pr}$ ), and  $\text{CH}=\text{CH}_2$  ( $\text{D}_4\text{Vin}$ ).

### Results and Discussion

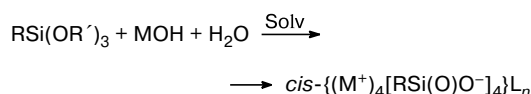
For the synthesis of new *cis*-tetra[(organo)(trimethylsiloxy)]cyclotetrasiloxanes *cis*- $[\text{RSi}(\text{O})\text{OSiMe}_3]_4$  ( $\text{R} = \text{Me, Et, Pr, Vin}$ ) we have prepared first the corresponding alkali organosiloxanates  $\{(\text{M}^+)_4[\text{RSi}(\text{O})\text{O}^-]_4\} \cdot n\text{L}$  ( $\text{M} = \text{Na, K}$ ;  $\text{L} = \text{R}'\text{OH, H}_2\text{O}$ ), whose main structural fragment

**Table 1.** Calorimetric characteristics of *cis*-tetra[(organo)(trimethylsiloxy)]cyclotetrasiloxanes

Tetramer	$-T_g$	$-T_{cr}^a$	$-T_1^b$	$-T_{m1}/-T_{m2}$	$\Delta C_p$ /J g <sup>-1</sup> K <sup>-1</sup>	$\Delta H_{cr}^c$	$\Delta H_m$	$\Delta H_1^d$
	°C							
D <sub>4</sub> Me <sup>e</sup>	>150	45	—	16.1/12.5	—	3.75	22.2	—
D <sub>4</sub> Vin <sup>e</sup>	118	79	—	17.5/9.0	0.11	2.81	16.5	—
D <sub>4</sub> Et <sup>f</sup>	—	—	87.5	22.1/16.5	—	—	18.6	2.2
D <sub>4</sub> Pr <sup>e</sup>	117	74	92.4	23.2/15.3	0.19	4.83	15.9	0.4

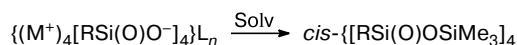
<sup>a</sup> Temperature of cold crystallization.<sup>b</sup> Isotropization temperature.<sup>c</sup> Enthalpy of cold crystallization.<sup>d</sup> Heat of isotropization.<sup>e</sup> For the first heating.<sup>f</sup> For the second heating.

is the cyclotetrasiloxanolate moiety *cis*-[RSi(O)O<sup>-</sup>]<sub>4</sub> as the starting compounds. Their synthesis is based on the hydrolytic condensation of the corresponding organo-trialkoxysilanes in the presence of an equimolar amount of sodium or potassium hydroxide (Scheme 1).\*

**Scheme 1**R = Me, Et, Pr, Vin; R' = Me, Et; M = Na, K; L = R'OH, H<sub>2</sub>O

Solv is solvent

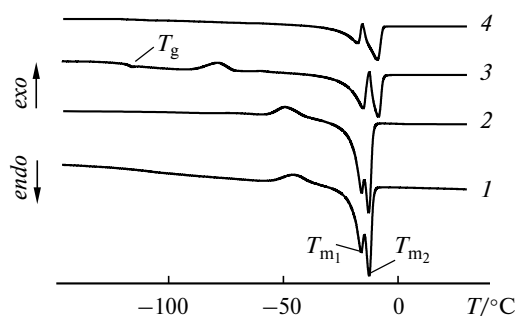
The subsequent reaction of alkali organosiloxanolates with trimethylchlorosilane makes it possible to remove the Na<sup>+</sup> or K<sup>+</sup> ions in the form of chlorides and isolate the corresponding *cis*-tetra[(organo)(trimethylsiloxy)]cyclotetrasiloxanes in high yield (Scheme 2).

**Scheme 2**R = Me, Et, Pr, Vin; L = MeOH, EtOH, H<sub>2</sub>O

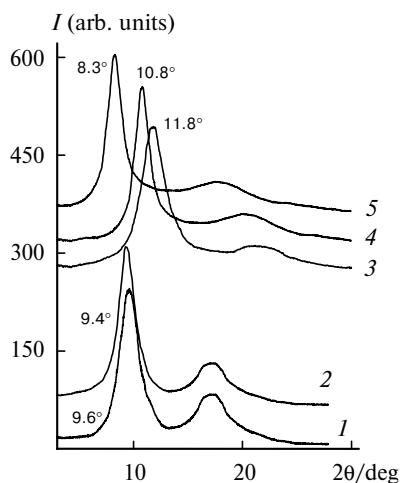
M = Na, K

The study of the thermotropic behavior of the synthesized cyclotetrasiloxanes showed that *cis*-[MeSi(O)OSiMe<sub>3</sub>]<sub>4</sub> and *cis*-[VinSi(O)SiMe<sub>3</sub>]<sub>4</sub> are crystallized compounds. According to the DSC (Fig. 1)

\* It has previously<sup>4</sup> been shown for phenyltrialkoxysilanes that this reaction can afford alkali siloxanolates in which the main fragment is the cyclotetra- and/or cyclotrisiloxanolate fragments and a set of oligomeric products. A certain choice of the reaction conditions makes it possible to direct the process to the formation of molecules of only one structural type.

**Fig. 1.** DSC curves for non-isomorphic cyclotetrasiloxanes D<sub>4</sub>Me (1, 2) and D<sub>4</sub>Vin (3, 4) on the first (1, 3) and second (2, 4) heating.

and X-ray diffraction (Fig. 2, curves 1 and 2) data, these two cyclotetrasiloxanes undergo the crystal → isotropic liquid transition forming no mesomorphic structures. At room temperature these compounds are colorless liquids. The DSC thermograms for D<sub>4</sub>Me and D<sub>4</sub>Vin are pre-

**Fig. 2.** X-ray diffraction of the liquid cyclotetrasiloxanes: D<sub>4</sub>Me (1), D<sub>4</sub>Vin (2), OMeCTS (3), Si(OSiMe<sub>3</sub>)<sub>4</sub> (4) at 20 °C, and Me<sub>3</sub>SiO[Si(OSiMe<sub>3</sub>)<sub>2</sub>O]<sub>4</sub>SiMe<sub>3</sub> (5) at 120 °C.

sented in Fig. 1, and the thermodynamic characteristics of the observed temperature transitions obtained from the DSC data are given in Table 1. It can be seen that the DSC curves of the both compounds on the first heating (see Fig. 1, curves 1 and 2) contain exotherms corresponding to cold crystallization, and the melting endotherms are multiplet. The presence of the exotherms indicates a low crystallization rate of these compounds and their partial transition to the isotropic glassy state on cooling. This is confirmed by the heat capacity jump detected for  $D_4\text{Vin}$  at  $T_g = -117$  °C (see Fig. 1, curve 3). In the case of  $D_4\text{Me}$ , no similar thermal effect was observed (see Fig. 1, curve 1). The glass-transition temperature of  $D_4\text{Me}$  is lower, most likely, than  $-150$  °C, indicating a decrease in the molecular mobility upon the replacement of the Me groups by more bulky vinyl groups. Upon repeated heating of  $D_4\text{Me}$  (see Fig. 1, curve 2), the exotherm corresponding to cold crystallization is retained, whereas for  $D_4\text{Vin}$  it is completely degenerate, as well as the heat capacity jump upon devitrification (see Fig. 1, curve 4). The position in the temperature scale and the total heat of the multiplet endothermic peaks corresponding to melting of the crystalline phase of cyclotetrasiloxanes remain unchanged upon repeated heating, although the ratio of their surface areas somewhat changes (see Fig. 1).

The diffraction patterns of cyclotetrasiloxanes  $D_4\text{Me}$  and  $D_4\text{Vin}$  obtained at room temperature (see Fig. 2) are typical of siloxane liquids; they contain two amorphous halos: the first, more intense halo is mainly responsible for intermolecular scattering, and its angular position  $2\theta_{a1}$  depends on the molecular size. The diffraction patterns of three siloxanes in the liquid state, *viz.*, OMeCTS and tetrakis(trimethyl)siloxysilane  $\text{Si}(\text{OSiMe}_3)_4$  (+) at 20 °C and decakis(trimethyl)siloxytetrasiloxane  $\text{Me}_3\text{SiO}[\text{Si}(\text{OSiMe}_3)_2\text{O}]_4\text{SiMe}_3$  (++++) at 120 °C, are presented in Fig. 2 (curves 3–5) for comparison. It is seen that an increase in the molecular volume in the order +  $\rightarrow$  OMeCTS  $\rightarrow$   $D_4\text{Me}$   $\rightarrow$   $D_4\text{Vin}$   $\rightarrow$  ++++ leads to the simultaneous shift of  $2\theta_{a1}$  to the small-angle region, *i.e.*, range of long intermolecular distances.

The DSC thermograms of cyclotetrasiloxanes with the Et and Pr groups are shown in Fig. 3, and the characteristics of the temperature transitions obtained by DSC are given in Table 1. The DSC thermogram (see Fig. 3, curve 1) for the primary heating of  $D_4\text{Et}$  contains two endotherms: the first, rather broad peak with a minimum at  $-17.5$  °C and the heat of melting  $\Delta H = 18.6$  J g $^{-1}$  and the second, narrower peak at 88 °C with  $\Delta H = 3.8$  J g $^{-1}$ . The DSC curve for the first heating of  $D_4\text{Pr}$  (see Fig. 3, curve 3) with the temperature increase exhibits the heat capacity jump for devitrification, bimodal exotherm corresponding to cold crystallization (see Table 1), endotherm with the heat of melting  $\Delta H = 16$  J g $^{-1}$  (see Table 1), and very weak endotherm with a minimum at 92 °C and  $\Delta H = 0.4$  J g $^{-1}$ . The low heat of the second endotherm

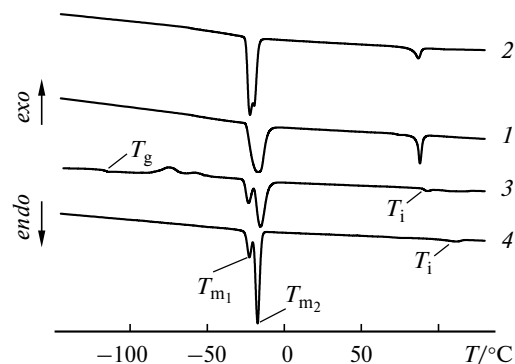


Fig. 3. DSC curves for the mesomorphic tetramers  $D_4\text{Et}$  (1, 2) and  $D_4\text{Pr}$  (3, 4) on the first (1, 3) and second (2, 4) heating.

compared to that of the first peak and the wax-like appearance of  $D_4\text{Et}$  and  $D_4\text{Pr}$  at 20 °C suggest that the second endotherm corresponds to the melting of the mesophase and its transition to the isotropic state. The  $\Delta H$  value found for the first *endo*-effect implies its correspondence to the crystal  $\rightarrow$  mesophase transition. The latter is confirmed by the X-ray diffractometry data (Fig. 4). Thus, unlike  $D_4\text{Me}$  and  $D_4\text{Vin}$ , cyclotetrasiloxanes with the Et and Pr groups transit to the mesomorphic state at a temperature exceeding the melting point of the crystalline phase.

On repeated heating, the DSC thermograms (see Fig. 3, curves 2 and 3) exhibit melting of the crystalline phase formed under the indicated conditions. This melting is two-stage for the both compounds. In this case, the heat of melting of the crystalline phase remains the same as that for the first heating, but for  $D_4\text{Et}$  the melting peak gains the bimodal character. The position of the high-temperature endotherm corresponding to the mesophase  $\rightarrow$  isotropic melt transition remains unchanged in the temperature scale for  $D_4\text{Et}$ ; however, the heat of melting decreases to 2.2 J g $^{-1}$ , whereas for  $D_4\text{Pr}$  the

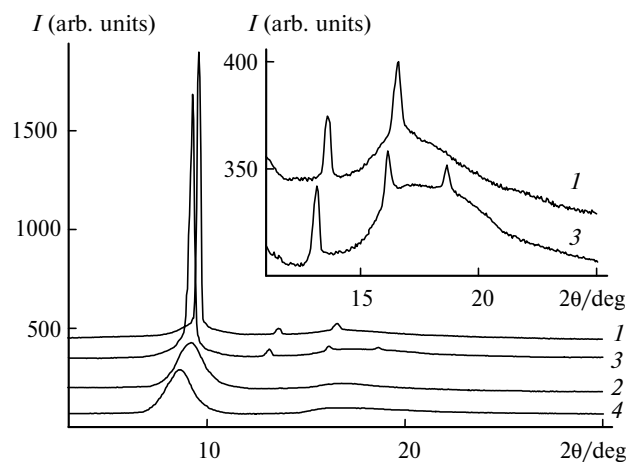


Fig. 4. X-ray diffraction of mesomorphic cyclotetrasiloxanes:  $D_4\text{Et}$  at 20 (1) and 85 °C (2);  $D_4\text{Pr}$  at 20 (3) and 120 °C (4).

isotropization temperature increases by 20 °C and the heat of this transition remains constant. These facts indicate the influence of the prehistory of cyclotetrasiloxane samples on the formation of the mesophase and its perfection. Bifurcation of the low-temperature transition can be explained by either different sizes and different degrees of perfection of crystallites, or the crystal → crystal structural transition.

At 20 °C the diffraction patterns of D<sub>4</sub>Et and D<sub>4</sub>Pr (see Fig. 4, curves 1 and 3) are typical of plastic crystals: they contain narrow ( $\Delta_{1/2} = 0.17^\circ$ ) peaks at  $2\theta = 9.59$  and  $9.29^\circ$  for D<sub>4</sub>Et and D<sub>4</sub>Pr, respectively, and low-intensity reflections at  $2\theta = 13.58$  and  $16.65^\circ$  for D<sub>4</sub>Et and at  $2\theta = 13.15$ ,  $16.13$ , and  $18.64^\circ$  for D<sub>4</sub>Pr. The angular position of the mesophase reflections is very temperature-sensitive. For instance, for the first peak of D<sub>4</sub>Et at  $T = 70$  °C the first reflection of the mesophase shifts to  $2\theta = 9.29^\circ$ , and for D<sub>4</sub>Pr at  $T = 82$  °C it shifts to  $2\theta = 9.13^\circ$ .

The ratio of the  $\sin^2\theta$  values for the adjacent peaks detected at 20 °C is 1 : 2 : 3 : 4, which suggests a cubic symmetry for the mesophase of D<sub>4</sub>Et and D<sub>4</sub>Pr. The latter was confirmed by optical polarization microscopy: at 20 °C the both compounds are optically isotropic.

The reflections detected for the mesophase of D<sub>4</sub>Et and D<sub>4</sub>Pr were indexed assuming all possible types of cubic cell, and the value of the packing coefficient  $k$  was a criterion for choosing the cell type.<sup>5</sup> It turned out that for these cycles only the packing coefficients calculated assuming the bcc cell fits the real  $k$  values for the mesomorphic state.

The peaks observed in the mesophase can be indexed as reflections 110, 200, and 211 (D<sub>4</sub>Et) and 110, 200, 211, and 220 (D<sub>4</sub>Pr) of three-dimensional bcc lattices; each bcc cell of D<sub>4</sub>Et and D<sub>4</sub>Pr contains two molecules. For D<sub>4</sub>Et at  $T = 20$  °C  $a = 13.03 \pm 0.05$  Å,  $V = 2210.74$  Å<sup>3</sup>,  $k = 0.58$ , and at  $T = 70$  °C, *i.e.*, near the isotropization point,  $a = 13.45 \pm 0.05$  Å,  $V = 2431.98$  Å<sup>3</sup>,  $k = 0.53$ . For

D<sub>4</sub>Pr at  $T = 20$  °C  $a = 13.51 \pm 0.05$  Å,  $V = 2463.95$  Å<sup>3</sup>,  $k = 0.58$ , and at  $T = 82$  °C, *i.e.*, near the isotropization point,  $a = 13.68 \pm 0.05$  Å,  $V = 2560.83$  Å<sup>3</sup>,  $k = 0.55$ .

According to the DSC (see Fig. 3, curves 1 and 2) and X-ray diffraction (see Fig. 4, curves 2 and 4) data, the transition of D<sub>4</sub>Et and D<sub>4</sub>Pr from the mesomorphic to isotropic state occurs at  $\sim 90$  and  $\sim 111$  °C, respectively. After isotropization the diffraction patterns contain only two broad maxima: a rather narrow amorphous halo ( $\Delta_{1/2} \approx 1.5^\circ$ ) at  $2\theta_{a1} = 9.16$  and  $8.60^\circ$  ( $d = 9.64$  and  $10.26$  Å) for D<sub>4</sub>Et and D<sub>4</sub>Pr, respectively, and a very broad and low-intensity halo at  $2\theta = 14$ – $26^\circ$ . Thus, the increase in the molecular volume in the order D<sub>4</sub>Me, D<sub>4</sub>Vin, D<sub>4</sub>Et, and D<sub>4</sub>Pr also reflects the distribution of the amorphous scattering intensity in the liquid state or melt.

Thus, the replacement in cyclotetrasiloxane D<sub>4</sub>Ph of four Ph groups by aliphatic groups changes considerably the temperature boundaries of mesophase existence: the processes of melting and isotropization shift to the region of lower temperatures and the temperature region of mesophase existence is strongly narrowed. With the elongation of the aliphatic framing, *i.e.*, on going from D<sub>4</sub>Et to D<sub>4</sub>Pr, the isotropization temperature increases and the temperature region of mesophase existence is extended.

As found in Ref. 3, molecules of the D<sub>4</sub>Ph cyclotetrasiloxane occupy nodes in the bcc cell of the mesophase of the plastic-crystalline type. The diffraction pattern of the D<sub>4</sub>Ph mesophase contains five reflections, and the bcc cell for the mesophase of this compound was determined rather reliably. Therefore, as additional checking of valid assignment of the cubic mesophase of D<sub>4</sub>Et to the bcc type, we studied a D<sub>4</sub>Et–D<sub>4</sub>Ph mixture with a weight ratio of 1 : 1.

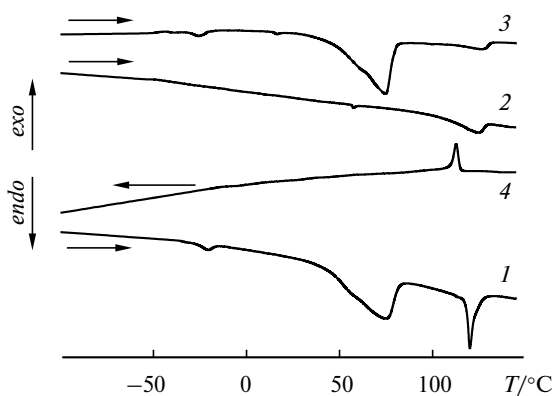
The DSC curves for a D<sub>4</sub>Ph–D<sub>4</sub>Et mixture are shown in Fig. 5, and the calorimetric characteristics of the ob-

**Table 2.** Temperatures ( $T/^\circ\text{C}$ ) and heats of phase transitions ( $\Delta H/\text{J g}^{-1}$ ) observed by the DSC method for D<sub>4</sub>Et, D<sub>4</sub>Ph, and their mixture in a weight ratio of 1 : 1 on heating and cooling

Object	Detection mode	Crystal → mesophase/mesophase → crystal		Mesophase → melt/melt → mesophase	
		$T_{\text{cr-meso}}/T_{\text{meso-cr}}$	$\Delta H_{\text{cr-meso}}/\Delta H_{\text{meso-cr}}$	$T_{\text{meso-s}}/T_{\text{s-meso}}$	$\Delta H_{\text{meso-s}}/\Delta H_{\text{s-meso}}$
D <sub>4</sub> Et	I heating/cooling	–17.5/–54.8	18.6/18.5	88.1/79.0	3.8/2.23
	II heating	–22.1 (–16.5)	18.6	87.5	2.2
D <sub>4</sub> Ph	I heating/cooling	80.0/19.0	28.5/27.6	265.0/248.0	4.6/4.2
	II heating	80.0	28.7	265.0	4.5
D <sub>4</sub> Et–D <sub>4</sub> Ph (1 : 1)	I heating/cooling	–21.0/–	0.8/–*	120.0/113.0**	2.7/1.5**
		74.2/–	20.8/–*		
	II heating	–/–	–/–	125.0/–**	1.6/–**
	III heating (after 90 h)	–25.1/–	0.6/–*	127.1/–**	1.5/–**
		74.0/–	21.0/–*		

\* Based on individual *cis*-tetra[(organo)(trimethylsiloxy)]cyclotetrasiloxane.

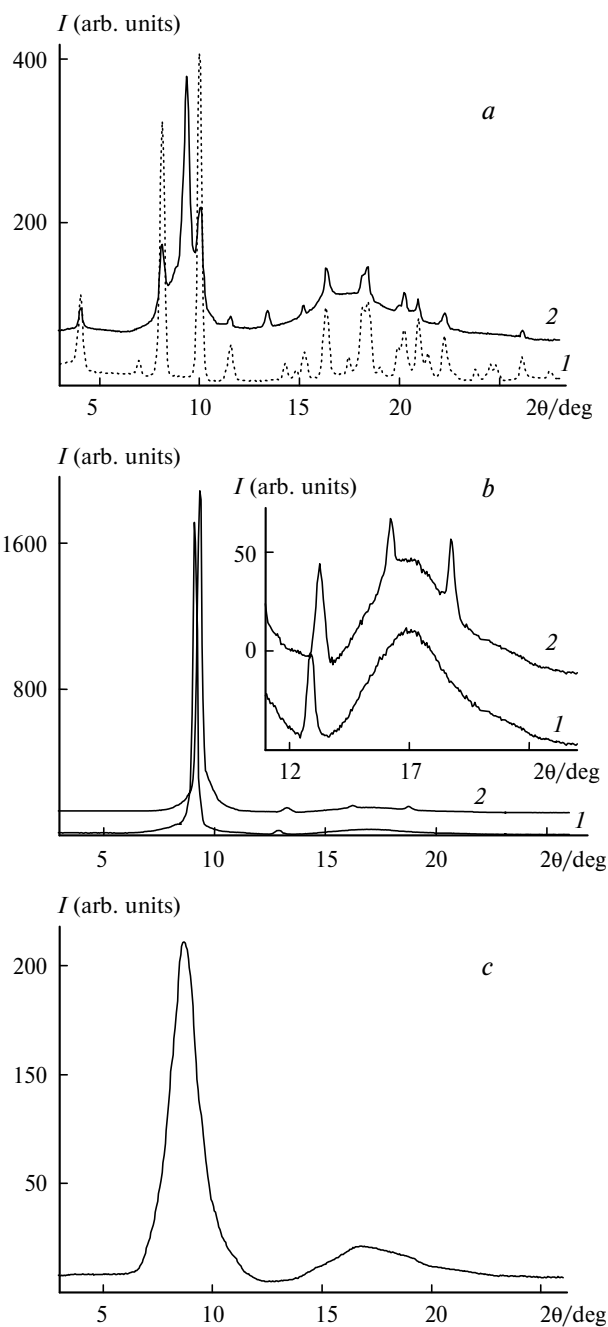
\*\* Combined mesophase.



**Fig. 5.** DSC curves for the  $D_4Et$ – $D_4Ph$  mixture (weight ratio 1 : 1) on heating (1–3) and cooling (4) with a rate of  $\pm 20$  deg  $min^{-1}$ : 1, 2, and 4, initial mixture; 3, sample after storing at 20 °C for 90 h.

served transitions are given in Table 2. The DSC curve of the initial mixture (see Fig. 5, curve 1), which was prepared as described in Experimental, contains three endotherms corresponding to consecutive melting of the crystalline phase of  $D_4Et$  and  $D_4Ph$  and isotropization of the mixture. It is seen from the data in Table 2 that the crystalline phase of  $D_4Et$  in the mixture is very deficient (crystallinity  $\leq 4\%$ ), and the crystallinity of  $D_4Ph$  is  $\sim 75\%$ . The principle of additivity of thermal effects is not either fulfilled for isotropization. However, as shown above, the heat of the mesophase  $\rightarrow$  isotropic melt transition for the individual  $D_4Et$  compound depends on the prehistory of mesophase formation.

The diffraction patterns of the  $D_4Ph$ – $D_4Et$  mixture obtained at different temperatures are presented in Fig. 6. The diffraction pattern of the initial mixture at 20 °C (see Fig. 6, a, curve 2) exhibits reflections of the  $D_4Ph$  crystals and a reflection of the  $D_4Et$  mesophase. On heating above the melting temperature of the crystalline phase of  $D_4Ph$ , *i.e.*, above 65 °C, the diffraction pattern contains only two reflections of the mesophase at  $2\theta = 9.09$  and  $12.88^\circ$  (see Fig. 6, b, curve 1), which confirms isomorphism of  $D_4Ph$  and  $D_4Et$  in the mesophase. Compared with individual  $D_4Et$  (see Fig. 4, curve 1), the angular position of the peak of the mixture mesophase (see Fig. 6, a, curve 2) shifts substantially to the small-angle region, reflecting the increase at 70 °C in the  $a$  parameter of the bcc cell to 13.74 Å. This increase is quite regular, because the replacement of the ethyl groups in cyclotetrasiloxane by the phenyl groups increases substantially the van der Waals volume of the molecule  $\Sigma\Delta V_1$  from 642.36 Å<sup>3</sup> to 804.52 Å<sup>3</sup>. The mesophase  $\rightarrow$  melt transition for the mixture is observed at  $T = 130$  °C. The diffraction pattern of the melt of the mixture (see Fig. 6, c) is qualitatively identical to that of the  $D_4Et$  melt; however, the maximum of the first amorphous halo is localized at  $2\theta = 8.72^\circ$  ( $d = 10.13$  Å,



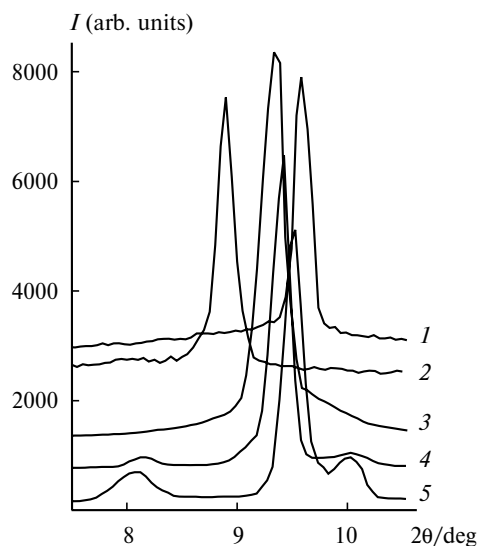
**Fig. 6.** X-ray diffraction of the individual  $D_4Ph$  (1) and initial  $D_4Et$ – $D_4Ph$  mixture (2) at 20 °C (a);  $D_4Et$ – $D_4Ph$  mixture (b) at 85 °C (1) and at 20 °C after cooling from melt, *i.e.*, from 130 °C (2); melt of a  $D_4Et$ – $D_4Ph$  mixture at 130 °C (c).

$\Delta_{1/2} = 1.5^\circ$ ), indicating higher values of the average intermolecular distances in the melt of the mixture compared to those in the  $D_4Et$  melt.

Immediately after cooling from melt below 20 °C, the mixture is mesomorphic and the peak of the mesophase is localized at  $2\theta = 9.33^\circ$  ( $a = 13.39$  Å) (see Fig. 6, b, curve 2). This value of the bcc cell parameter is also much

higher than that for  $D_4Et$ . The DSC thermogram on cooling of the mixture (see Fig. 5, curve 4) contains only an exotherm corresponding to mesophase formation, and upon repeated heating only a broad endotherm peak corresponding to isotropization is observed (see Fig. 5, curve 2). Thus,  $D_4Ph$  crystallization in a mixture is difficult (on cooling of individual  $D_4Ph$  under similar conditions, crystallization is observed at 26 °C). However, as can be seen from the data in Fig. 7,  $D_4Ph$  in a mixture crystallizes gradually with time. The mesophase peak systematically shifts to the large-angle region, indicating a decrease in the  $a$  parameter of the bcc cell. Therefore, at 20 °C the mesophase of the mixture is gradually enriched in  $D_4Et$  molecules due to  $D_4Ph$  crystallization. The diffraction pattern of the mixture 90 h after cooling from melt coincides completely with the diffraction pattern of the mixture obtained by recrystallization from solution (see Fig. 6, *a*, curve 2). The angular position of the mesophase peak corresponds to the similar value of the individual  $D_4Et$  compound. Analogous changes are observed for the DSC curves (see Fig. 5, curve 3). Note, however, that no additivity is observed for the heat of transitions, as well as for heating of the primary mixture (see Table 2), indicating considerable steric hindrance for the formation of the perfect crystalline phase by each component.

The results obtained for the  $D_4Ph$ – $D_4Et$  mixture indicate both identity of the structural organization of these cyclotetrasiloxanes in the mesophase (bcc cell) and high mobility of these molecules in the mesophase, providing their high diffusion rate and processes of microphase separation, which occur despite the high mo-



**Fig. 7.** Fragments of the diffraction patterns for the  $D_4Et$  mesophase at 20 °C (1),  $D_4Ph$  mesophase at 87 °C (2), and  $D_4Et$ – $D_4Ph$  mixture at 20 °C after cooling from melt in 1 (3), 54 (4), and 72 h (5).

bility of the molecules and result finally in the true phase separation.

Thus, the replacement of all phenyl groups in cyclotetrasiloxane  $[RSi(O)OSiMe_3]_4$  ( $R = Ph$ ) by methyl or vinyl groups suppresses the mesomorphic properties. The introduction of ethyl or propyl groups as organic substituents recovers the ability of cyclotetrasiloxane to undergo the transition to the mesomorphic state. However, on going from  $R = Ph$  to  $R = Et$  and  $Pr$ , the temperature boundaries of mesophase existence change substantially: the melting and isotropization temperatures shift to the low-temperature region and the temperature region of mesophase existence becomes substantially narrower. When the aliphatic framing elongates, *i.e.*, on going from  $R = Et$  to  $R = Pr$ , the isotropization temperature increases and the temperature region of mesophase existence is broadened.

Similar regularities of changing the mesomorphic properties are observed<sup>6</sup> with variation of the type of side framing for cyclotetrasiloxanes and known linear mesomorphic polyorganosiloxanes  $[-O-Si(R_2)-]_n$ . This specific feature of the compounds manifests itself, although the structures of their mesophases are different. Mesophases of polyorganosiloxanes are of the 2D-columnar type, and the compounds under study are characterized by the plastic-crystalline phase of the 3D type. In fact, the polymeric order with  $R = Me, Et, Pr,$  and  $Ph$  possesses the same affinity to mesomorphism and tendency for changing the mesomorphic properties as the series of tetramers  $cis-[RSi(O)OSiMe_3]_4$  with  $R = Me, Et, Pr,$  and  $Ph$ .

One more important regularity should be mentioned. Symmetrically substituted cyclotetrasiloxanes  $[RSi(O)R]_4$ , *viz.*, OEtCTS and OPrCTS, have no mesomorphic properties. Breaking of the "up-and-down" symmetry in these cyclotetrasiloxanes by the replacement of some aliphatic groups by the  $Me_3SiO$  groups results in the appearance of mesomorphic properties. Pairs of cyclotetrasiloxanes OEtCTS– $cis-[EtSi(O)OSiMe_3]_4$  and OPrCTS– $cis-[PrSi(O)OSiMe_3]_4$  manifest regularities close to those found previously for the OPhCTS– $[PhSi(O)OSiMe_3]_4$  pair. Thus, the absence of "up-and-down" symmetry in the cycles can be considered as one of the factors affecting the capability of mesomorphic ordering and mesomorphic properties.

## Experimental

Alkyltrialkoxysilanes  $MeSi(OEt)_3$ ,  $VinSi(OEt)_3$ ,  $EtSi(OEt)_3$ , and  $PrSi(OMe)_3$ , trimethylchlorosilane (Aldrich), and NaOH and KOH (analytical grade) were used. Solvents were prepared according to earlier described procedures.<sup>7</sup>

$^1H$ ,  $^{13}C$ , and  $^{29}Si$  NMR spectra were recorded on a Bruker AMX spectrometer ( $^1H$ , 400.1 MHz;  $^{13}C$ , 100.1 MHz;  $^{29}Si$ , 79.5 MHz) at 20 °C in  $CDCl_3$ .

DSC studies of *cis*-tetra[(organo)(trimethylsiloxy)]cyclo-tetrasiloxanes were carried out on a Mettler-822e differential scanning calorimeter with a heating rate of 20 deg min<sup>-1</sup> under argon. The first heating was conducted after preliminary cooling of a sample in the calorimeter cell to -150 °C with a rate of 20 deg min<sup>-1</sup>, and the second heating was carried out after cooling to -150 °C with a rate of 10 deg min<sup>-1</sup>. The position of the minimum (maximum) of the peak in the DSC thermogram was accepted to be the transition temperature.

A Dron-3M diffractometer (Cu-K $\alpha$  radiation, bent quartz single crystal as a focusing monochromator) equipped with a high temperature chamber (accuracy of temperature maintenance  $\pm 1$  °C) was used for X-ray diffraction studies. Diffraction patterns were obtained in the transmission detection mode.

A POLAM-213M polarization microscope was used for optical studies.

**Potassium *cis*-tetramethylcyclotetrasiloxanolate (1).** Hexane (21 mL) and KOH (1.65 g, 0.025 mol) were charged in a three-neck flask equipped with a stirrer and reflux condenser with a calcium chloride tube. The mixture was stirred, and MeSi(OEt)<sub>3</sub> (4.48 g, 0.025 mol) and a mixture of water (0.45 mL, 0.025 mol) with EtOH (3 mL) were added. The reaction mixture was stirred for 1.5 h at ~20 °C. After several hours at +4 °C, a finely crystalline white substance precipitated from the solution. The precipitate was filtered off, washed with hexane, and dried on a rotary evaporator (40 °C, 10 Torr) to a constant weight. A white crystalline powder was obtained in a yield of 2.37 g (73%). Found (%): C, 13.90; H, 3.60; K, 30.29; Si, 21.66. {(K<sup>+</sup>)<sub>4</sub>[MeSi(O)O<sup>-</sup>]<sub>4</sub>·EtOH·H<sub>2</sub>O, C<sub>6</sub>H<sub>20</sub>K<sub>4</sub>O<sub>14</sub>Si<sub>4</sub>, molecular weight 521. Calculated (%): C, 13.83; H, 3.87; K, 30.02; Si, 21.56.

**Potassium *cis*-tetravinylcyclotetrasiloxanolate (2).** A white crystalline powder was synthesized similarly from VinSi(OEt)<sub>3</sub> (9.027 g, 0.047 mol), KOH (3.13 g, 0.047 mol), and H<sub>2</sub>O (0.08 mL, 0.004 mol) in a hexane-EtOH (42 mL + 6 mL) mixture in a yield of 5.09 g (74%). Found (%): C, 21.05; H, 4.05; K, 26.39; Si, 19.07. {(K<sup>+</sup>)<sub>4</sub>[C<sub>2</sub>H<sub>3</sub>Si(O)O<sup>-</sup>]<sub>4</sub>·EtOH·2H<sub>2</sub>O, C<sub>10</sub>H<sub>22</sub>K<sub>4</sub>O<sub>11</sub>Si<sub>4</sub>, molecular weight 587. Calculated (%): C, 20.46; H, 3.78; K, 26.64; Si, 19.14.

**Sodium *cis*-tetra(*n*-propyl)cyclotetrasiloxanolate (3).** Anhydrous EtOH (57 mL), NaOH (1.12 g, 0.028 mol), Pr<sup>n</sup>Si(OMe)<sub>3</sub> (4.66 g, 0.028 mol), and H<sub>2</sub>O (0.50 mL, 0.031 mol) were charged in a three-neck flask with a stirrer, reflux condenser, and calcium chloride tube. The reaction mixture was stirred under reflux for 30 min. The solvent was removed on a rotary evaporator, and the resulting product was dried to a constant weight (40 °C, 10 mm Hg). A white crystalline powder was obtained in a yield of 3.85 g (100%). Found (%): C, 30.74; H, 6.08; Na, 16.36; Si, 20.11. {(Na<sup>+</sup>)<sub>4</sub>[C<sub>3</sub>H<sub>7</sub>Si(O)O<sup>-</sup>]<sub>4</sub>·EtOH, C<sub>14</sub>H<sub>34</sub>Na<sub>4</sub>O<sub>9</sub>Si<sub>4</sub>, molecular weight 550. Calculated (%): C, 30.53; H, 6.22; Na, 16.70; Si, 20.40.

**Trimethylsilylation of synthesized alkali organosiloxanolates (general procedure).** Hexane, trimethylchlorosilane, and pyridine were charged in a three-neck flask equipped with a stirrer, reflux condenser, and calcium chloride tube. Then alkaline metal siloxanolate was added with stirring. The reaction mixture was brought to boiling, refluxed for 1 h with stirring, and then cooled to ~20 °C, and a precipitate that formed was filtered off. The filtrate was washed from Cl<sup>-</sup> ions (probe with AgNO<sub>3</sub>). The solution was dried above Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed

under reduced pressure (rotary evaporator, 60 °C, 10 mm Hg and then at 60 °C, 1 mm Hg).

***cis*-Tetra[methyl(trimethylsiloxy)]cyclotetrasiloxane (D<sub>4</sub>Me).** The target product (1.87 g, 69%) as a colorless liquid was synthesized from siloxanolate **1** (2.37 g, 4.5 mmol), trimethylchlorosilane (5.64 g, 0.052 mol), and pyridine (2.46 g, 0.031 mol) in hexane (30 mL). <sup>1</sup>H NMR,  $\delta$ : 0.055 (s, 3 H, O<sub>3</sub>SiMe); 0.136 (s, 9 H, OSiMe<sub>3</sub>); the ratio of integral intensities of signals from the protons of OSiMe<sub>3</sub> and O<sub>3</sub>SiMe being 3 : 1. <sup>13</sup>C NMR,  $\delta$ : -2.84 (s, O<sub>3</sub>SiMe); 1.56 (s, OSiMe<sub>3</sub>). <sup>29</sup>Si NMR ( $\delta$ : -66.72 (s, O<sub>3</sub>SiMe); 8.78 (s, OSiMe<sub>3</sub>).

***cis*-Tetra[vinyl(trimethylsiloxy)]cyclotetrasiloxane (D<sub>4</sub>Vin).** The target compound (2.22 g, 40%) as a colorless liquid was synthesized from compound **2** (5.09 g, 8.6 mmol), trimethylchlorosilane (9.42 g, 86.7 mmol), and pyridine (4.16 g, 0.052 mol) in hexane (35 mL). <sup>1</sup>H NMR,  $\delta$ : 0.161 (s, 9 H, OSiMe<sub>3</sub>); 5.847–5.987 (m, 3 H, C<sub>2</sub>H<sub>3</sub>); the ratio of integral intensities of signals from the protons of OSiMe<sub>3</sub> and C<sub>2</sub>H<sub>3</sub> being 3 : 1. <sup>13</sup>C NMR,  $\delta$ : 1.70 (s, OSiMe<sub>3</sub>); 132.21 (s, CH=C<sub>2</sub>H<sub>3</sub>); 134.66 (s, C<sub>2</sub>H=C<sub>2</sub>H<sub>3</sub>). <sup>29</sup>Si NMR,  $\delta$ : -80.58 (s, O<sub>3</sub>SiC<sub>2</sub>H<sub>3</sub>); 10.09 (s, OSiMe<sub>3</sub>).

***cis*-Tetra[*n*-propyl(trimethylsiloxy)]cyclotrisiloxane (D<sub>4</sub>Pr).** The target product (6.77 g, 95%) as a colorless viscous liquid was synthesized from compound **3** (5.59 g, 0.0135 mol), trimethylchlorosilane (9.15 g, 0.084 mol), and pyridine (3.48 g, 0.044 mol) in hexane (80 mL). <sup>1</sup>H NMR,  $\delta$ : 0.131 (s, 9 H, OSiMe<sub>3</sub>); 0.507 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 0.965 (t, 3 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.350–1.446 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); the ratio of integral intensities of signals from the protons of OSiMe<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, and CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> being 9 : 2 : 3 : 2. <sup>13</sup>C NMR,  $\delta$ : 1.81 (s, OSiMe<sub>3</sub>); 16.64 (s, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 16.77 (s, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 17.85 (s, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>29</sup>Si NMR,  $\delta$ : -68.60 (s, O<sub>3</sub>SiPr<sup>n</sup>); 8.28 (s, OSiMe<sub>3</sub>). Signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra were assigned on the basis of data of the 2D COSY-45 and HSQC GP experiments.

**Sodium *cis*-tetraethylcyclotetrasiloxanolate and *cis*-tetra[(ethyl)(trimethylsiloxy)]cyclotetrasiloxane (D<sub>4</sub>Et)** were synthesized according to a previously described procedure.<sup>8</sup>

**Mixture D<sub>4</sub>Et–D<sub>4</sub>Ph (weight ratio 1 : 1).** A mixture of cyclotetrasiloxanes was heated for 1 h in a sealed ampule under argon to 180 °C, then cooled to ~20 °C with a rate of ~2 deg min<sup>-1</sup>, and stored for 12 h at -5 °C.

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