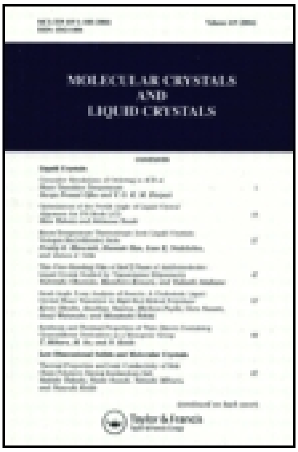

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Structure Investigations of Thermotropic Liquid Crystalline Monomer and Polymer Organosilicon Compounds

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STRUCTURE INVESTIGATIONS OF THERMOTROPIC LIQUID CRYSTALLINE MONOMER AND POLYMER ORGANOSILICON COMPOUNDS

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Abstract Structures of monomolecular siloxane derivatives forming mesophase due to the presence of the one-dimensional system of hydrogen bonds are described on the basis of X-ray investigations of LC and TC phases. X-ray investigations of related polymer compounds was used as a ground for polymer structure modeling on an atomic level.

INTRODUCTION

Classical thermotropic compounds are as a rule composed of rod-like or disk-like molecules. The presence of polar groups, which could form hydrogen bonds, usually prevents formation of liquid crystalline phases, but sometimes the formation of hydrogen bound aggregates (i.e. dimers) does not stop mesophase formation [1,2]. Recently a series of organosilicon compounds with unusual (for liquid crystalline compounds) molecular shape and hydroxyl groups, which are able to form various systems of H-bonds, was synthesized [3]. Formation of polymer LC phases, in which traditional mesophase fragments are also absent, are quite common for organosilicon compounds [4].

The aim of this work was to figure out the main features of LC structure of monomer and polymer siliconorganic compounds. In order to solve this problem X-ray analysis of solid crystalline and LC samples, spectroscopic investigations of all phases, and computational molecular modeling were used.

MONOMERIC ORGANOSILOXANE MESOGENS

Thermotropic mesomorphism has been found in the series of organosilicon compounds 1,3-di-hydroxytetraalkyldisiloxanes $[R_2(OH)Si]_2O$, $R=n\text{-}C_nH_{2n+1}$, $n \geq 2$ [3]. Temperatures (^oC) of the phase transitions are as follows:

R	n-Bu	n-Pr	Et
T(TC-LC)	17.1	35.0	-36.0
T(LC-L)	53.5	64.0	37.0

X-ray investigations have shown that all these mesophases are characterized by the hexagonal two-dimensional unit cells. Related compounds with R=Me, i-Pr and Ph do not form LC phase. Such investigations do not give the possibility to obtain the detailed structure of the mesophase, therefore the X-ray investigation of solid crystalline precursors of LC phase was performed. These investigations allowed to obtain information about the system of hydrogen bonds in the crystal. Spectroscopic studies enabled us to find out if hydrogen bond system changes during phase transitions.

We investigated crystal structures of 1,3-di-hydroxytetra-alkyldisiloxanes with R=Me, Et, n-Pr [5-7] and compared our results with the related compounds with R=i-Pr and Ph, which were studied earlier [8,9]. Crystal data of the abovementioned compounds are summarized in Table 1. The mutual feature of these compounds is the presence of several

TABLE 1 Crystal data of mesogenic and related non-mesogenic organosilicon compounds $R_2(OH)SiOSi(OH)R_2$

R	a	b	c	α	β	γ	Sp.g.	Z
n-Pr	13.073	19.98	21.26	90.05	83.09	88.09	$P\bar{1}$	12
Et	9.57	13.84	20.38	90.0	92.32	90.0	$P2_1/n$	8
Me	8.442	5.792	19.308	90.0	91.67	90.0	$P2_1/n$	4
i-Pr	8.968	9.008	21.898	82.21	89.69	85.08	$P\bar{1}$	4
Ph	15.231	13.472	20.293	99.51	73.05	120.86	$P\bar{1}$	6

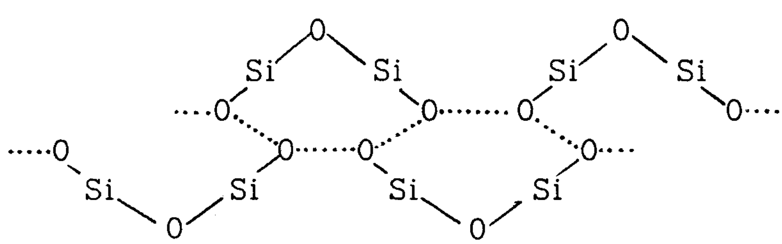
systems of symmetrically independent molecules in the crystal. Symmetrically independent molecules are characterized by various conformations, which can be described by the pseudotorsion angles between hydroxyl groups (Table 2). We are inclined to think that the presence of various confor-

TABLE 2 Conformational characteristics of organosilicon molecules $R_2(OH)SiOSi(OH)R_2$

R	Angles, degree Si-O-Si		(H)OSi...SiO(H)	
n-Pr	145.0;	144.8;	-92;	70;
	166.9;	166.9;	-70;	94;
	165.4;	164.4	-69;	70
Et	147;	151	95;	96
Me	140.1		-81	
i-Pr	164.3;	163.8	40.2;	51.2
Ph	156.8;	161.9;	68.6;	-70.0
	147.6		-63.6	

mations in TK precursors of LC phases at least in part reflects the real structure of mesophase, in which molecular conformations are resembling liquid phase conformations.

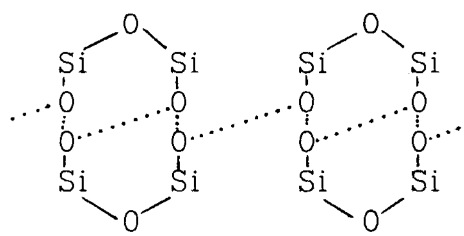
Another common peculiarity of these compounds is the presence of infinite one-dimensional molecular aggregates formed by hydrogen bonds, shown on the scheme:



The cores of the aggregates (or columns) are formed by the polar oxygen-containing groups, and the external surface of columns by non-polar hydrocarbon chains. These aggregates are characterized by rod-like shape and form nearly hexagonal packing in crystal. The parameters of hexagonal pseudo-cell of the mesogenic crystals and mesophase are similar:

R	n-Pr	Et
a(cr.),Å	12.66	10.69
a(mes.),Å	12.58	11.10

It is worth mentioning that in these columns hydrogen bonds form infinite system of cooperative nearly equivalent hydrogen bonds. Mesophase was not found in i-Pr substituted compound where one-dimensional aggregates are built of dimeric moieties:



Mesophase was also not found for Me- and Ph-substituted compounds. In our opinion it is probably due to the rigidity of the external surfaces of the molecular columns.

These results enable us to conclude that a new structural type of thermotropic LC phase was in fact found. On the basis of our investigations we suggest that other compounds which form one-dimensional hydrogen bonded aggregates in crystal may form similar structures in mesophases. On the base of conformational calculation of free molecules and comparison of geometrical parameters of columns, we suggest mesophase formation for compounds $R_2M(OH)X(OH)MR_2$, where X=O, S, CH_2; M=Si, Ge. We also believe that the 3-mono- or 3,4,5-trialkyl- or alkoxysubstituted phenols, which often form one-dimensional H-bonded aggregates in crystals, will exhibit similar mesogenic properties.

POLYMER ORGANOSILICON THERMOTROPIC COMPOUNDS

The related class of polymer compounds, which form thermotropic LC phase recently was synthesized [4]. There are cyclolinear polyorganosiloxanes with various cycle size and various organic substituents, which form the surface of polymer molecules. These polymers have been attracting considerable attention due to their ability to form mesophases without traditional mesogenic groups.

The methylsubstituted polymers from this class, i.e. poly[oxy(hexamethylcyclotetrasiloxy-2,6-diyl)]siloxane (HMTS) are characterized by its steep tacticity dependence of the ability to form the ordered phases [4,10]. New method of synthesis [11] gives the possibility to obtain a series of HMTS with various chain tacticity including high trans-tactic samples (σ=trans/cis=88/12). With the help of NMR ^{29}Si the stereospecificity of the reaction of heterofunctional condensation and the conformation of the polymer chain was characterized [11]. The characteristics of polymer tacticity are shown in Table 3.

TABLE 3 Characteristics of tacticity of HMTS

Sample	$[\eta]$ dl g^{-1}	μ_W 10^3	Isomer composition of initial *trans/cis,%	monomers **trans/cis,%	Ratio of polymer units trans/cis,%
I	0.17	55.0	97/3	100/0	66/34
II	0.06	84.6	98/2	100/0	88/12
III	0.23	42.6	98/2	100/0	88/12

*dichlorohexamethylcyclotetrasiloxane;
**dihydroxyhexamethylcyclotetrasiloxane

In order to estimate the phase content of PMTS near the isotropization temperature T_i, diffractograms of samples II and III at different temperatures have been obtained (Fig.

1). No significant changes of the temperature of phase transition on varying MM were found.

On heating up to 70°C the number of the observed reflections decreases. At 74°C only four sharp reflections still remain (Fig.1a). Their sin2θ values ratio is equal to 3:4:13:16. This ratio together with temperature dependence of the reflections show the existence of two-dimensional ordering in the basal plane of mesophase I. On further heating from 75°C to T_i=108°C the smearing of the X-ray pattern in the angular region 2θ=14-30° was detected. Simultaneously the two first reflections show a trend to coalesce into one. These changes are disguised by the process of isotropization, but one can assume the availability of polymesomorphic transition of mesophase I to II near the temperature of isotropization. The temperatures of phase transitions obtained by X-ray analysis are in a good agreement with the DSC data [10].

The unambiguous evidence of the structural rearrangement just before T_i has been obtained by investigation of the quenched sample. It is obvious (Fig. 2) that high temperature mesophase is partly quenched after rapid cooling of the sample. The diffractograms of the quenched PMTS samples reveal an additional third reflexion, which confirms the existence of high temperature mesophase II.

Mesophase II characterized by hexagonal arrangement of polymer molecules and two-dimensional unit cell with a=9.88Å. The phase transition II-I is accompanied by lowering the symmetry of the unit cell and by increasing the number of molecules per unit cell. In this case the two-dimensional rectangular unit cell with Z=2 is most probable. During the transition to the high-ordered phase (+20°C) the additional reflections in the range 2θ=14-30° can be observed for samples II and III (Fig.1b). Smearing of the X-ray pattern observed for sample I in the angular region 2θ=14-30° can be attributed both to the influence of distortions of the second order and to the lack of long-

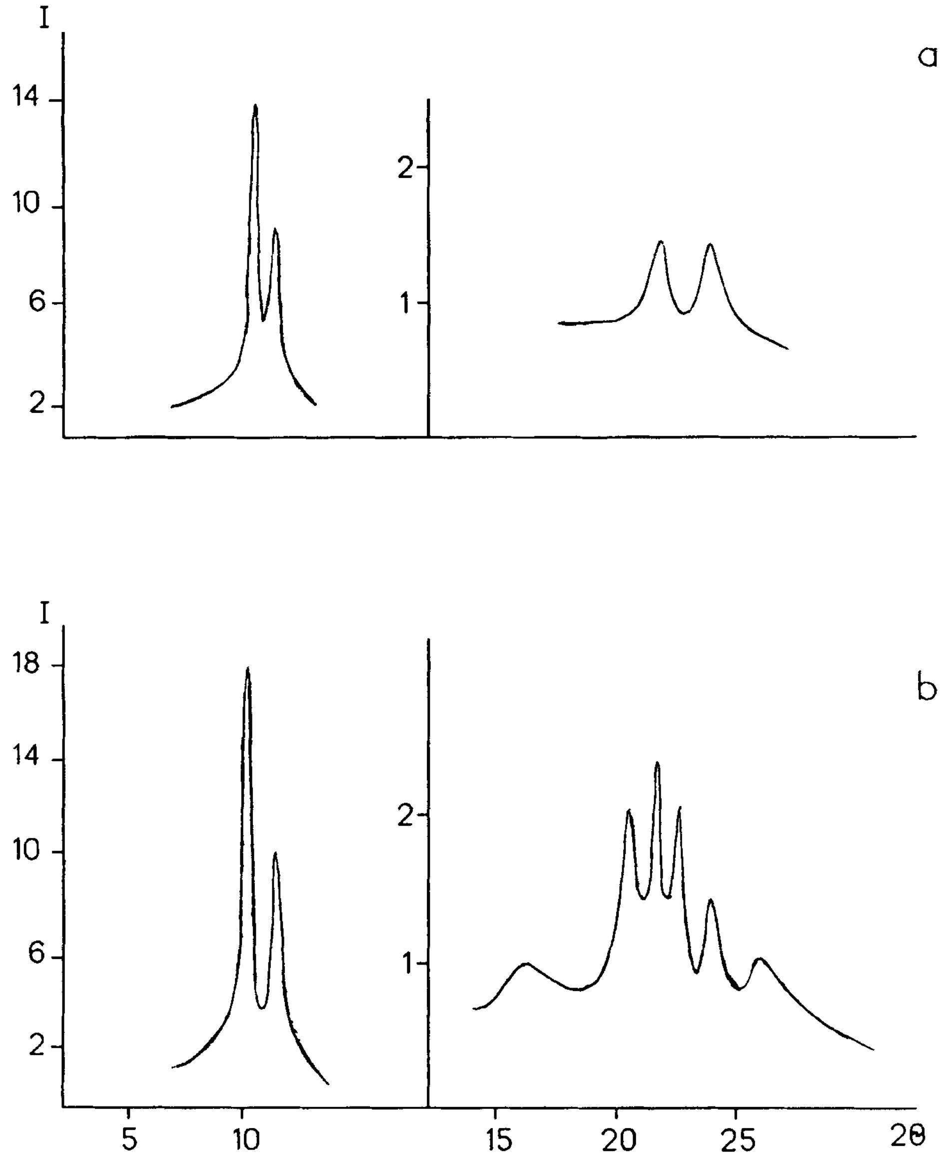


FIGURE 1 Diffractograms of sample II obtained at different temperatures: a 74°C; b 12°C

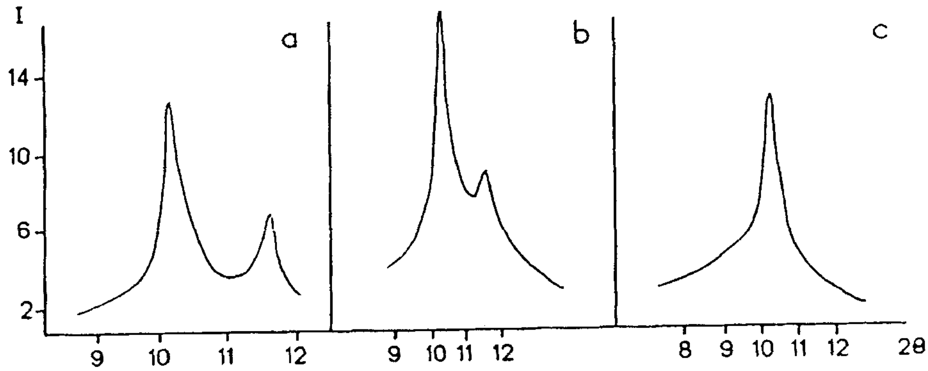


FIGURE 2 Diffractograms of the quenched sample II obtained at different temperatures: a 20°C; b 86°C; c 95°C

range ordering along the main chain. The latter assumption is more likely taking into account the small changes in the basal plane during the phase transition. Some sets of possible rectangular unit cell parameters for the samples II and III were found.

The way to characterize the structure of the polymer on atomic level is to model its idealized structure in atom-atom approximation. The first part of such modeling is calculation of conformations of isolated polymer units and then the fragments of polymer chain. The second part of modeling is the packing of polymer chains in crystal with the lowest crystal lettice energy. It is usually on the second stage that the experimental crystal data are used.

Computational modeling of polymer structure was performed on IBM PC/286 using POLYM program, whose algorithms were described in detail in [12]. The cell parameters of two-dimensional unit cell, obtained by X-ray analysis of polymer samples were used for the modeling of HMTS.

The conformations of polymer unit and fragment of polymer chain obtained by energy minimization are shown in Figure 3. During this stage of minimization positions of all atoms were varied. We use chain model with two units

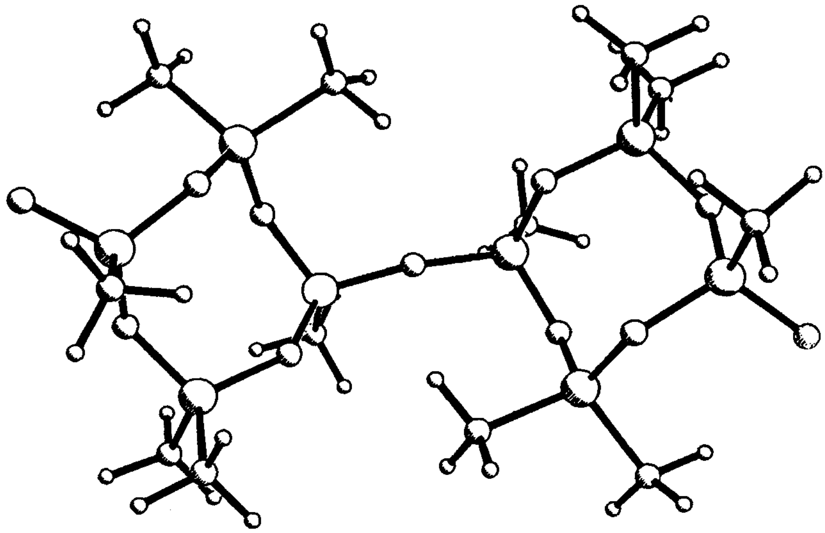


FIGURE 3 Computed structure of polymer chain fragment

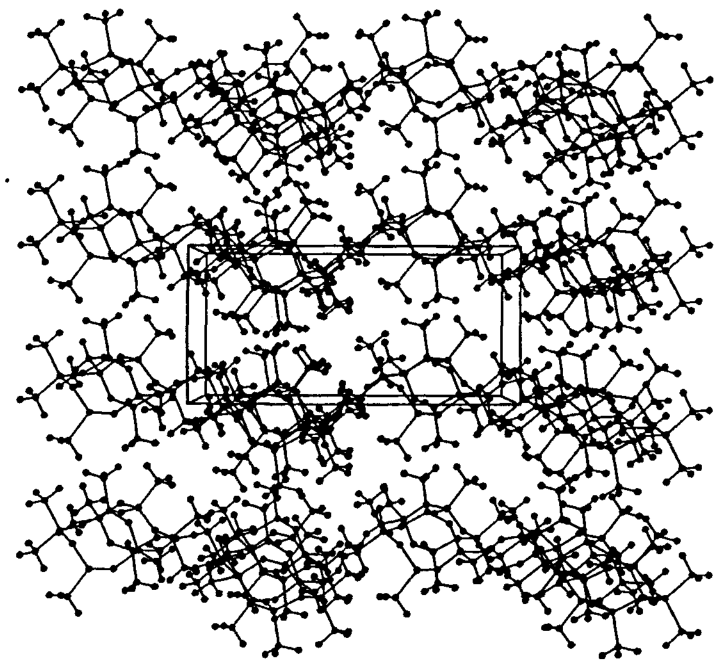


FIGURE 4 Packing of HMTS molecules in crystal

per a period for minimization of polymer lattice energy. One of the most probable rectangular unit cells (a=17.27, b=8.43 Å) derived from X-ray analysis was used for modeling. In the process of crystal minimization we varied the orientation of methyl groups and bond angle at the O bridging atom in the polymer chain. We varied also the positions of chains in the unit cell and their relative orientation. Space group $P2_1$ appears to be the most favourable for the packing of the polymer molecules. Cell parameter along the axis of this molecule was found to be 13.63 . Crystal packing of HMTS is shown in Figure 4. The energy of reorientation of PMTS molecule around the long axis was found to be ca. 10 kcal/mol. The calculation of the other energy characteristics associated with relative displacement of polymer molecules in crystal are in progress.

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