Liquid crystalline carbosilane dendrimers: first generation

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Intramolecular microsegregation: a driving force of nanostructure formation in liquid-crystalline dendrimers

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A Commentary on the paper "Liquid crystalline carbosilane dendrimers: First generation",
by S. A. Ponomarenko, E. A. Rebrov, A. Yu. Bobrovsky, N. I. Boiko, A. M. Muzafarov and
V. P. Shibaev. First published in *Liquid Crystals*, **21**, 1–12 (1996).

It was a very special task to read anew and comment on a paper of your own published twenty years ago - especially as many results and their interpretations usually become obsolete after such a long time. The scientific community has gained new knowledge, from the stand point of which the old papers seem not as interesting as at the moment of completing the work and publishing a report on it. At the same time it is pleasant to note, that the main conceptions of the 1996 *Liquid Crystals* paper related to the elaboration of the synthesis, studies of phase behaviour and the structure of liquid-crystalline dendrimers have found not only a good verification in our further and "foreign" works, but provided an additional powerful impetus (incentive) to the development of this promising scientific area.

Actually, from the beginning of the 1990s liquid-crystalline dendrimers have had a growing scientific interest as viewed from the point of view of researchers working in such fields as the chemistry and physics of liquid crystals, the physico-chemistry of macromolecular compounds and supramolecular chemistry. At the present time the compounds with dendritic architecture including liquid-crystalline dendrimers are being assigned as the principal objects of nanomaterials and nanotechnology.

In the nineties, our main efforts were focused on the elaboration of methods for the synthesis of liquid-crystalline dendrimers of different generations containing terminal mesogenic groups (see figure 1 of our 1996 paper). The molecular structure of dendrimers is, in many respects, similar to the branched comb-shaped (side-chain polymers), containing long aliphatic chains in each monomer unit [1–3]. It is well-known that the comb-shaped polymers offered a convenient matrix for

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the creation of the first thermotropic liquid-crystalline polymers synthesized by us [4] and the German group [5] independently of each other. In such systems the side mesogenic groups (modeling mesogenic fragments of low-molar-mass liquid crystals) were linked to the macromolecular backbone by flexible (e.g. aliphatic) spacers. The concept of the spacer, originally introduced in our work, inspired the development of a new direction of research related to the creation of thermotropic comb-shaped liquid-crystalline polymers.

Practically the same principle was implemented, for the first time, by us [6] for the synthesis of a poly(organosiloxane) dendrimer with terminal cholesterol groups attached via undecylene spacers to a dendritic methylsesquioxane matrix:
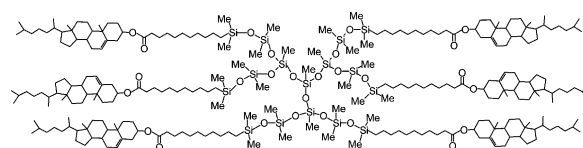
In essence, this compound is a typical liquid-crystalline dendrimer of the first generation containing six terminal cholesterol mesogenic groups, that displays a smectic A mesophase over a broad temperature range (from $-1.5°C$ to $120°C$). The results of this research were presented, for the first time, by myself, in 1994 at the International Conference on Liquid Crystalline Polymers in Beijing (China).

In a like manner the general strategy and approach to the synthesis of a novel family of carbosilane liquid-crystalline dendrimers has been developed by our scientific team from Moscow State University together with Muzafarov's group from the Institute of Synthetic Polymer Materials of the Russian Academy of Sciences. This approach, described in the 1996 paper includes
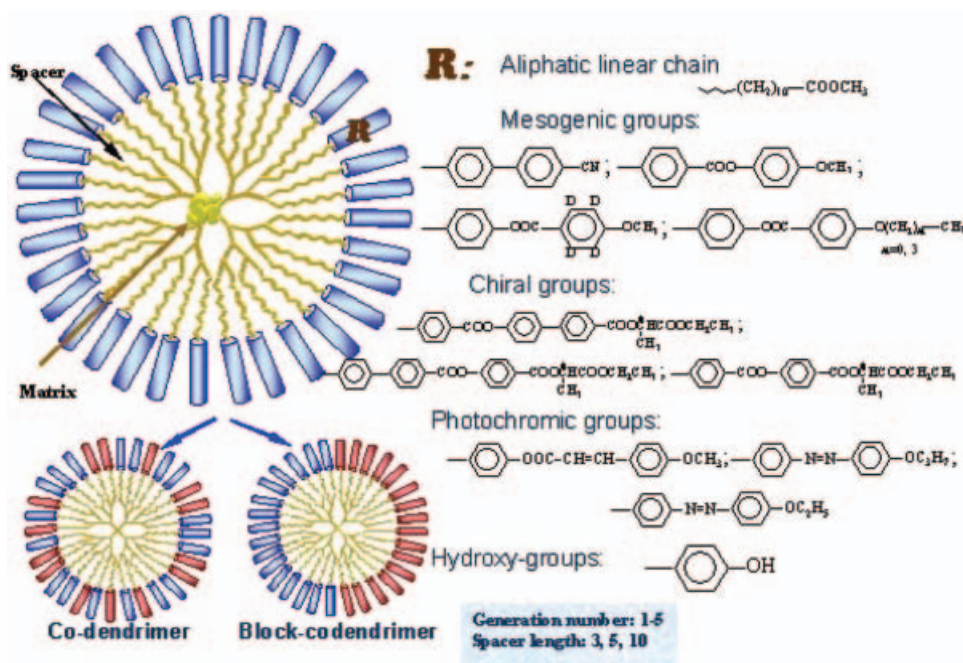
Figure 1. General molecular structure of liquid-crystalline dendrimers (G-3) with different mesogenic groups and molecular constitution of statistical and block-codendrimers.

three main steps: (1) synthesis of a dendritic matrix with terminal carbon–carbon double bonds; (2) synthesis of the mesogen-containing fragment with a spacer and terminal reactive hydrogen atom (mesogenic monomer); (3) chemical coupling of the mesogenic monomer to the dendritic matrix by a hydrosilylation reaction.

The paper reprinted here and the paper already cited [6] initiated the subsequent synthesis and study of ball-shaped dendritic molecules which can be considered as a separate class of liquid-crystalline compounds. Actually the incorporation of mesogens into a dendritic archi-tecture is an intriguing design approach which can result in the fabrication of hybrid structures combining liquid-crystalline properties and dendritic functionalities and shapes. The interest in the investigations of liquid-crystalline dendrimers is dictated by their unusual exotic structure. Each dendritic molecule can be represented in the form of a sphere, the internal part of which consists of a superbranched matrix core. The external part or periphery of the dendritic molecule consists of mesogenic fragments chemically linked to the core by a spacer (containing methylenic groups) of different length.

The main features of liquid-crystalline dendrimers distinguishing them from linear polymers are defined by their regular superbranched topology, low polydispersity, absence of entanglements and the large number of terminal mesogenic groups. Similar to the two-faced Janus, liquid-crystalline dendrimers clearly demonstrate the dual nature of their physico-chemical properties. On the one hand, dendritic molecules have on average spherical symmetry and tendency to acquire an isotropic spatial distribution in a vacuum. This is a typical entropic factor inherent to macromolecules. On the other hand, the rigid rod-like mesogens tend to form an anisotropic phase due to a large gain in the enthalpy. This is a typical energetic factor inherent to liquid crystals. As a result of these contradictory tendencies, a phase-separated and self-assembled structure had to be formed. In other words, the class of structure formation in liquid-crystalline dendrimers should be the result of microse-gregation followed by self-assembly of the mesogenic fragments. In fact, liquid-crystalline dendrimers are original hybrids combining macromolecular properties of a superbranched matrix and the properties of low-molar-mass liquid crystals.

Starting with the 1996 *Liquid Crystals* paper, describing only the first generation of liquid-crystalline dendrimers, in succeeding years we synthesised a series of all five generations, G, of dendrimers containing 16(G-2), 32(G-3), 64(G-4) and 128(G-5) mesogenic groups. Among them, the classical alkyl- and alkoxy-phenylbenzoate derivatives, cyanobiphenyl groups, deuteriated alkoxyphenylbenzoates, chiral mesogenic groups with different disposition of benzene and biphenyl groups, photochromic azobenzene and cyan-nomoyl fragments, as well as a number of non-

mesogenic groups – aliphatic chains and hydroxyl-containing structural units. As an example, figure 1 shows the general molecular structure of a liquid-crystalline dendrimer of the third generation demonstrating the existence of a mesogenic shell around a central nucleus, formed by the soft carbosilane dendritic matrix.

The approaches to the synthesis of carbosilane liquid-crystalline dendrimers described in our early publications were later verified and developed in work performed in Germany, Japan, Spain and the United Kingdom. The 1990s can be considered as a period of the liquid-crystalline dendrimer boom. Hundreds of new liquid-crystalline dendrimers with different dendritic cores such as, polyesters, poly(propylene imine), polysiloxane, polyurethane, poly(amidoamine) were synthesized in the laboratories of various countries. Since that time the investigations of structure, physico-chemical behaviour of liquid-crystalline dendrimers in the bulk, in dilute solutions and gels were widely presented in the literature. New theoretical approaches to the description of liquid-crystalline dendrimer structure and its simulation came into being.

The first major review of liquid-crystalline dendrimers was published in *Polymer Science* in 2001 by us [7]; it summarized both the data available in the literature and the results of original investigations performed by our group. A short time later the special issue of *Journal of Materials Chemistry*, related to the molecular topology in liquid crystals including papers on structural peculiarities of liquid-crystalline dendrimers was

published [8] and we can recommend this issue of the Journal to our readers.

One of the most important questions arising during the analysis of the physico-chemical properties of liquid-crystalline dendrimers is related to their supra-molecular structure based on their molecular constitution, that is the number of branching points (generation number, G), the chemical nature of the matrix, number and the chemical structure of the mesogenic groups, spacer length, etc. The elucidation of the definite correlations between the molecular/supramolecular structure of liquid-crystalline dendrimers and their properties as well as the prediction of their mesophase types and behaviour of liquid-crystalline dendrimers under the action of different external fields (such as electric, magnetic, mechanical, light irradiation) reasoning from theoretical grounds are of considerable interest for the continuation and development of research associated with liquid-crystalline dendrimers. As for the carbosilane liquid-crystalline mesogen-containing dendrimers it should be pointed out that the presence of a long spacer in any dendritic molecule, suggested by us in the 1996 paper, always facilitates liquid-crystalline phase formation; in addition, its lengthening essentially increases the liquid-crystalline temperature range for the existence of the mesophase. As a rule longitudinal linking of mesogenic groups to dendritic matrices of low generation (G-1 – G-3) leads to the formation of layer structures, for example, SmA and SmC. Lateral bonding of mesogens with dendritic cores usually favours nematic phase formation. Increasing generation
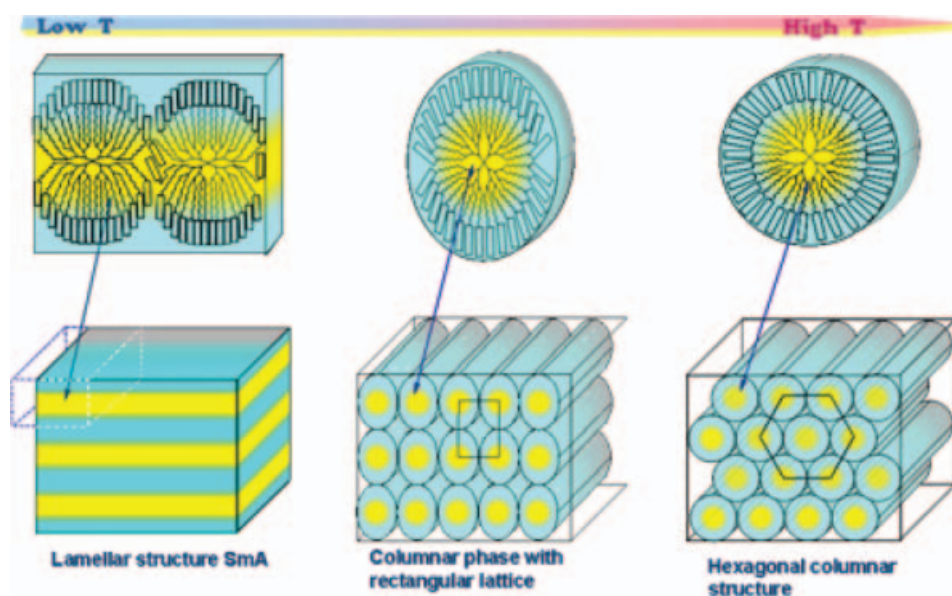

Figure 2. Schemes of dendritic molecules and their organisation in the smectic mesophase, orthogonal and hexagonal columnar mesophases for carbosilane liquid-crystalline dendrimers (G-5).

number (G>3) with a longitudinal linkage forces the dendritic matrix to adopt a more spherical shape and, as a result, the transition from smectic structure to columnar phase takes place. Moreover, the formation of a columnar mesophase can be realized for the fifth generation of liquid-crystalline dendrimers at high temperature (where the entropic role of a matrix is clearly manifested), while the smectic mesophases are formed at low temperatures. Figure 2 shows the proposed models of dendritic molecules and their organisation in different polymorphic modifications at different temperatures. It is clearly seen how the initial layer structure, consisting of alternating dendritic cores and mesogenic groups, is transformed into a hexagonal columnar structure consisting of more symmetrical dendritic molecules.

In a series of publications related to dendron molecules various authors [8] have discovered the formation of columnar and cubic mesophases, in which the main contribution to segregation results from the incompatibility of the different fragments of the branched molecules. It is very important to stress that in all dendritic systems such as those mentioned, the self-organization process based on micro-segregation is driven by the association of like parts of the dendritic compounds which tend to avoid the dissimilar parts of the same molecules.

Synthetic chemists continue to surprise us, synthesizing novel families of liquid-crystalline dendrimers with complex and unusual architecture such as fullerene- and ferrocene-containing liquid-crystalline dendrimers, banana and other bent-shaped dendritic molecules, chiral nematic octasilsesquioxanes, ferroelectric as well as a number of metal-containing liquid-crystalline

dendrimers. Mesogenic fragments included in the dendritic structure have demonstrated a great tendency to self-assemble into a rich variety of different liquid-crystalline superstructures with nanoscale dimensions through the combination of shape complementarity and the repulsive interaction of rigid and flexible parts as an organizing force. The mesophases include smectic, hexagonal columnar, bicontinuous cubic, honeycomb-like and different discrete micellar phases.

It is our great pleasure to say that our 1996 *Liquid Crystals* paper was one of the pioneering papers in the field of liquid-crystalline dendrimers and marked the beginning of active research in this intriguing field of liquid crystals.

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Liquid crystalline carbosilane dendrimers: first generation

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An approach to the synthesis of a new class of liquid crystalline (LC) compounds, dendrimers of regular structure with terminal mesogenic groups, was elaborated. LC dendrimers based on the carbosilane dendritic matrix of first generation were synthesized. Cyanobiphenyl, methoxyphenyl benzoate and cholesteryl groups were used as mesogenic fragments. Individuality and structure of all compounds obtained was proved by GPC together with ^{1}H- and ^{29}Si NMR methods. The mesomorphic behaviour and structure of the LC dendrimers synthesized were investigated. It is argued that different mesophases of the smectic type are realized in all cases. It is shown that the mesophase type of these compounds essentially depends on the chemical nature of the mesogenic groups.

1. Introduction

A new field of chemistry of high molecular mass compounds associated with the synthesis of three-dimensional superbranched polymers and oligomers, called dendrimers, has recently been actively developed [1]. Obtaining these compounds is very interesting, because each elementary act of a molecule's growth is accompanied by an increase in the number of branching points in geometrical progression. As a result, the shape and rigidity of the molecules are changed with increase in the molecular mass. That, as a rule, leads to strong variations in the physico-chemical properties of dendrimers, such as their characteristic viscosity, solubility [2], density [3], phase transitions, etc.

Present-day synthetic approaches permit the production of the so-called regular dendrimers, macromolecules of which have a strictly determined molecular mass. In addition, many properties of dendrimers such as glass transition temperature [4], solubility and others, depend mainly on the chemical nature of the terminal groups which are located, as a rule, on the surface of such ballshaped molecules. All the above-mentioned have stimulated great interest among researchers in the synthesis of dendritic macromolecules [3, 5–11].

In the literature there is some information concerning the synthesis of dendritic block copolymers containing hydrophobic phenyl 'surface' groups on one half of the 'molecular-ball' and hydrophilic carboxylic groups on

the other half [12], or with electron-withdrawing CN-groups on one half and electron-donating benzyl ether groups on the other half [13]. Moreover, many other publications have indicated the wide possibilities of molecular design of dendritic macromolecules.

Some time ago we suggested an approach to the synthesis of a new type of dendrimer [14–17]—liquid crystalline (LC) dendrimers (figure 1). They differ from those described earlier in the literature [18, 19] by the fact that the mesogenic groups, responsible for realization of the LC state, are disposed only on a 'surface' layer of dendritic macromolecules of regular structure.

We consider such LC dendrimers as very interesting materials for investigation for the following main
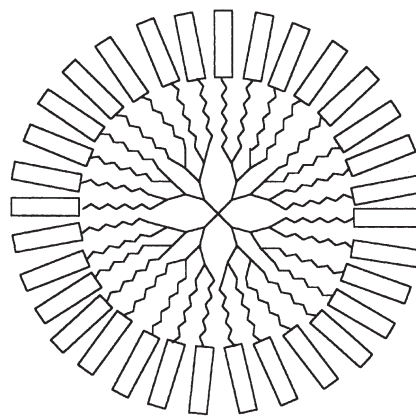

Figure 1. Schematic representation of the molecular structure of the LC dendrimer.

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reasons. First, the unusual, exotic character of the molecular structure of such compounds should be noted; each superbranched molecule can be represented as a sort of sphere, the internal part of which consists of non-mesogenic blocks while the outside surface of the sphere is formed by the mesogenic fragments. Such a 'microheterogeneous' structure of the molecules should predetermine a tendency of the dendritic systems to microphase separation, just as it takes place in block and graft copolymers, as well as in some comb-shaped polymers [20]. In this sense, the study of the structural organization of dendrimers consisting of heterogeneous blocks, part of which tends to give LC phase formation, presents a subject of essential scientific interest from the structural point of view, bearing in mind their molecular and supermolecular organization.

The possibility of the creation of an LC shell ('jacket') around a central nucleus, formed by the 'soft' dendritic matrix, is also interesting from the practical point of view. It opens up perspectives for the application of such compounds as active structural modifiers which can be introduced into usual polymers for the modification of their mechanical, rheological and tribological properties, as well as for the creation of selective membranes and drug delivery systems.

There are at least two fundamentally different approaches to the synthesis of dendrimers. The first is based on uncontrolled reactions of low molecular mass compounds that lead to the formation of branched molecules from, as a rule, a trifunctional monomer. In this case all three functional groups participate in the reaction growth, forming a dendrimer whose molecular mass and dimensions are determined by the reactivity of the intermediates and a number of kinetic factors.

The second method, called usually the controlled synthesis, is based on the sequential assembly of individual molecular fragments using a layer-by-layer synthetic method via reiterative sequences of reactions of lower 'growth' with protection and deprotection of reactive groups. The merits of this method have been well proved by the multi-step synthesis of cholesteryl-containing polyorganosiloxane dendrimers of regular structure which have been described for the first time in the literature [14, 15].

Having in mind the elucidation of 'structure-properties' relationships for LC dendrimers, till now practically non-existent, we associate the goal of the present publication and future work in this field with the synthesis and systematic study of LC dendrimers of different but regular molecular structure.

In accordance with [14, 15] we have now extended our approach to the synthesis of new LC dendrimers based on the carbosilane dendritic matrix containing different mesogenic groups, as shown below:

$$Si_{21}^{8}[(CH_2)_{10}COO\text{-}Mes]$$
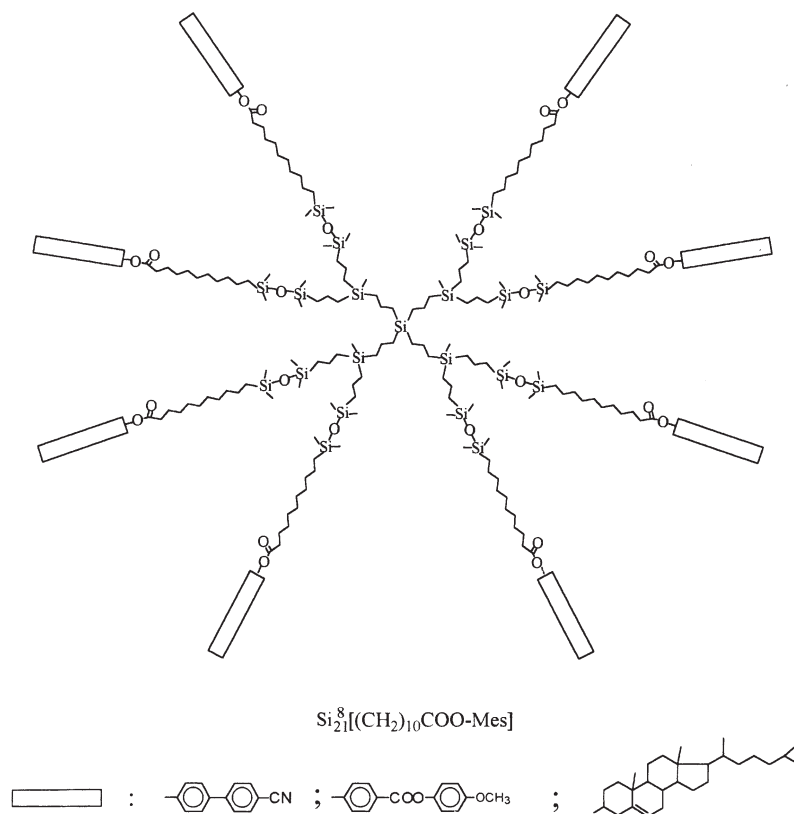
This paper presents a detailed description of the synthesis of the three different new dendrimers of the first generation[†], containing only eight mesogenic groups, and our preliminary data on their structure and phase behaviour.

2. Results and discussion

2.1. *General strategy of the synthesis of LC dendrimers*

Elaborating the universal approach to the synthesis of dendrimers of regular structure with terminal mesogenic groups, we have concentrated our attention on two important points. First, we had to choose such a chemical reaction of the matrix with the mesogen-containing compound, which would permit us to obtain LC dendrimers without occurrence of side-chain reactions and formation of by-products. Second, the reaction between the matrix and mesogenic fragments should be controlled in order to obtain the target dendrimers with strictly defined molecular mass. Finally, the mesogenic groups should be completely 'indifferent' with respect to the chemical reactions used for their attachment to the dendritic matrix.

Taking into account all the above mentioned points, hydrosilylation, satisfying all the enumerated conditions [21], was chosen as the base reaction. Using this reaction, some carbosilane dendrimers [10, 22] have been successfully synthesized recently, and that is why we also decided to choose this reaction for synthesis of LC dendrimers. The structure of the initial carbosilane dendritic matrix $Si_8^5(Allyl)$[‡] is shown below.
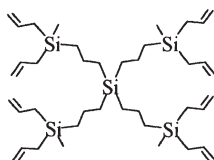
The detailed method of synthesis of this dendrimer has been described previously [23]. In figure 2 the synthetic route to the synthesis of the dendritic matrix is briefly summarized.

In our work we have started with the carbosilane dendrimer of the smallest generation ($G=1$) owing mostly to its availability, and the simplicity of isolation and identification of final products. However it does not limit the universality of the elaborated synthetic approach; using the same synthetic route, subsequent generations of LC dendrimers can be synthesized.

[†] According to Tomalia and Durst [1], generations are defined as stepwise reiterative reaction sequences in controlled dendrimer synthesis.
[‡] In the formula $Si_x^y(Z)$: x is the number of silicon atoms in the dendritic molecule; y is the number of terminal groups Z, shown in the parentheses.
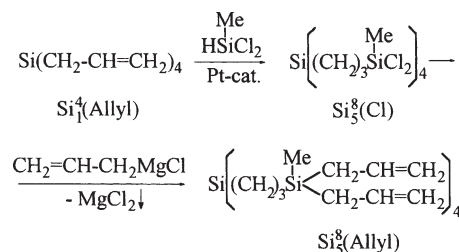

Figure 2.   Scheme of synthesis of the dendritic matrix.

As can be seen from figure 2, the selected carbosilane dendritic matrix contains terminal allyl groups. To attach the mesogenic groups to the matrix via hydrosilylation, it was necessary to modify them so that they would contain terminal Si–H groups capable of reacting with the allyl groups of the initial dendrimer. Taking into account experience in the synthesis of LC side chain (comb-shaped) polymers with mesogenic side groups which are often chemically linked to a polysiloxane main chain via methylene spacers [24, 25], we have used the same spacer-concept. Hence the mesogen-containing fragment for coupling to the carbosilane dendritic matrix should consist of the following structural units: mesogenic group (Mes), flexible spacer and terminal Si–H group, capable of reacting with the terminal allyl groups of dendritic matrix:
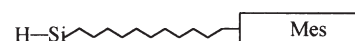
2.1.1. Synthesis of mesogen-containing fragment with Si–H terminal group.
The synthetic route for obtaining the mesogen-containing fragment with a reactive Si–H terminal group is briefly summarized in figure 3. Taking into account that the properties of liquid crystal materials essentially depend on the chemical nature of their mesogenic fragment, as well as with a view to checking the generality of the synthetic route suggested, we have used three types of the mesogenic groups—cyanobiphenyl, methoxyphenyl benzoate and cholesteryl—differentiated by their polarity and chirality.

As is seen from figure 3, the synthesis includes three stages, reactions (1)–(3). The undecylenic esters containing the above-named mesogenic groups (compounds **Ia**, **Ib** and **Ic**, respectively) were prepared according to standard method by acylation of the appropriate phenol or alcohol with the acid chloride of 10-undecylenic acid, reaction (1). The temperatures of the phase transitions of the compounds obtained coincide with early published data [26, 27] (table 1).

The esters of 11-(dimethylchlorosily1)undecanoic acid (compounds **IIa**, **IIb** and **IIc**) were obtained by

$$CH{=}CH_2(CH_2)_8\overset{O}{C}{-}Cl \ + \ HO{-}\boxed{Mes}$$

$$\downarrow \begin{array}{c} + \ N(Et)_3 \ , \\ THF \end{array} \quad -N(Et)_3{\cdot}HCl\!\downarrow \qquad (1)$$

$$CH{=}CH_2(CH_2)_8\overset{O}{C}{-}O{-}\boxed{Mes} \qquad \text{Ia, Ib, Ic}$$

$$\downarrow \begin{array}{c} + \ Cl\!-\!\overset{Me}{\underset{Me}{Si}}\!-\!H \end{array} \quad \text{Pt-cat.} \qquad (2)$$

$$Cl\!-\!\overset{Me}{\underset{Me}{Si}}\!-\!(CH_2)_{10}\overset{O}{C}{-}O{-}\boxed{Mes} \qquad \text{IIa, IIb, IIc}$$

$$\downarrow \begin{array}{c} + \ H_2O \ ; \ + \ Py \ ; \\ + \ H\!-\!\overset{Me}{\underset{Me}{Si}}\!-\!Cl \end{array} \quad -Py{\cdot}HCl\!\downarrow \qquad (3)$$

$$H\!-\!\overset{Me}{\underset{Me}{Si}}\!-\!O\!-\!\overset{Me}{\underset{Me}{Si}}\!-\!(CH_2)_{10}\overset{O}{C}{-}O{-}\boxed{Mes} \qquad \text{IIIa, IIIb, IIIc}$$

where $\boxed{Mes}$ =

a) ⬡⬡–C≡N   **CB**

b) ⬡–COO–⬡–OCH₃   **MPhB**

c) [steroid structure] **Chol**

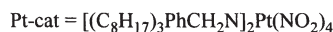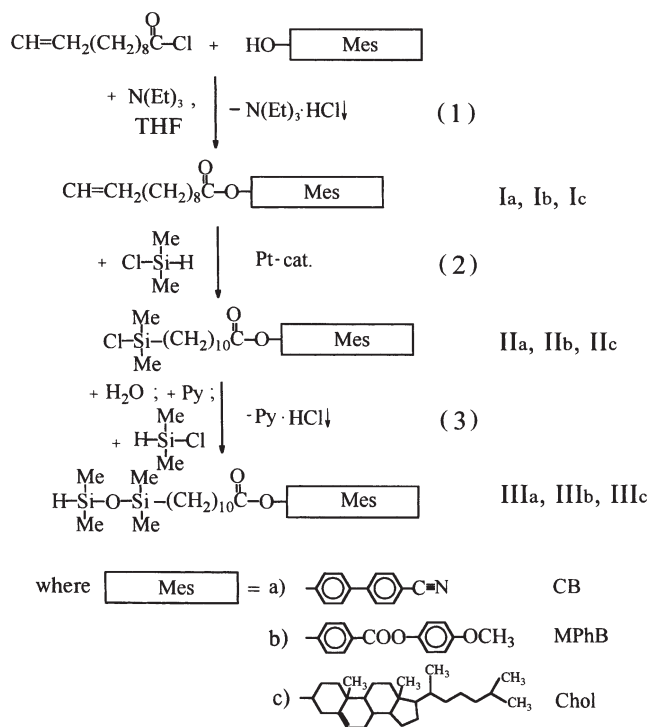Pt-cat = $[(C_8H_{17})_3PhCH_2N]_2Pt(NO_2)_4$

Figure 3. Scheme of synthesis of mesogen-containing fragments with reactive terminal groups.

the hydrosilylation of compounds **Ia**, **Ib** and **Ic** with dimethylchlorosilane in the absence of solvent. Bis(*N*,*N*,*N*-trioctylbenzy1amino)tetranitroplatinum was used as a catalyst (Pt-cat., see reaction (2) in figure 3). The completion of the reaction was checked by infrared (IR) and proton magnetic resonance (PMR) spectroscopy. In the IR spectra of the reaction products, the disappearance of the band for the stretching vibrations of the terminal carbon-carbon double bonds in the region $1640\,cm^{-1}$ was observed. Simultaneously, the appearance of the absorption band in the region $1260\,cm^{-1}$ corresponding to the stretching vibration of the Si–CH₃ bond was detected. Unlike the PMR spectra of the initial esters **Ia**, **Ib** and **Ic**, the PMR spectra of compounds **IIa**, **IIb** and **IIc** (see table 2) exhibit no signals due to protons of the terminal carbon–carbon double bond (doublet at $\delta_1 = 5.2\,ppm$ and multiplet at

$\delta_2 = 6.0\,ppm$). These results proved the fact that hydrosilylation was complete.

It is necessary to note that the cholesteryl ester of 10-undecylenic acid (compound **Ic**) contains two double bonds: the terminal double bond in the undecylenic fragment and the double bond in the steroid nucleus. However, in ref. [14] it is shown that hydrosilylation proceeds selectively at the terminal double bond, not affecting the nucleus of cholesteryl.

In the PMR spectra of compounds **IIa**, **IIb** and **IIc**, the singlet of the protons of the methyl groups at the silicon atoms is displayed in the region 0.4 ppm, and the multiplet signal of the protons of the methylene groups at the silicon atoms in the region 0.9 ppm. The ratios of the integral intensities of the proton signals correspond to the calculated values (see table 2).

Compounds **IIIa**, **IIIb** and **IIIc** were prepared by the cohydrolysis of compounds **IIa**, **IIb** and **IIc**, respectively, using a $40\times$ molar excess of dimethylchlorosilane and stoichiometric quantities of pyridine and water (calculated on the total amount of chlorosilicone groups). These conditions almost totally excluded the undesired process of homocondensation of the mesogen-containing molecules. The use of a large excess of dimethylchlorosilane provided a high yield of the final product and facilitated its isolation from the reaction mixture. The by-product, tetramethyldisiloxane, is a highly volatile substance. The yields of chromatographically pure products at this stage were 70–80%.

The IR spectra of the silanes **IIIa**, **IIIb** and **IIIc** show a narrow intense absorption band in the region $2100\,cm^{-1}$, corresponding to the stretching vibration of Si–H groups. The PMR spectra (see table 2) of these compounds display the appearance of multiplet signal for proton at silicon atoms in the region 4.9 ppm and a doublet signal for methyl protons at Si–H in the region 0.3 ppm. The ratio of the integral intensities of the signals due to methyl protons at the different silicon atoms corresponds to the calculated value of 1:1.

2.1.2. Synthesis of carbosilane dendrimers with mesogenic groups. Coupling of the mesogen-containing fragments to the dendritic carbosilane matrix $Si_8^5(Allyl)$ was carried out by hydrosilylation in the presence of

Table 1. Phase transitions of the intermediate compounds **Ia**, **Ib** and **Ic** (see figure 3).

Compound	Temperature of phase transitions/°C	
	This work	Published data
$CH_2{=}CH{-}(CH_2)_8{-}COO{-}CB$ (**Ia**)	Cr 51 S_A 66 N 71 I	Cr 50 S_A 67 N 73 I [27]
$CH_2{=}CH{-}(CH_2)_8{-}COO{-}MPhB$ (**Ib**)	Cr 56 N 70 I	Cr 57 N 74 I [27]
$CH_2{=}CH{-}(CH_2)_8{-}COO{-}Chol$ (**Ic**)	Cr 73 (S 66) Ch 82 I	Cr 72 S 77 Ch 81 I [26]

Table 2.   Chemical shifts of proton signals in the **PMR** spectra compounds **I–IV (a**, **b**, **c**). Note: s is singlet, d is doublet, т is triplet, m is multiplet. Here and in the text the figure before H is the number of hydrogen atoms.

| Compound	Chemical shifts δ/ppm.										
	Si–CH$_3$		Si–CH$_2$–		–CH$_2$–	Si–H		CH$_2$=CH–		Ar–H	
Ia	—	—	—	1.5(m,10H) 1.9(m,2H)	2.2(m,2H)	2.8(т,2H)	—	5.2(d,2H)	6.0(m,1H)	7.2(d,2H)	7.7(m,6H)
IIa	—	0.4(s,6H)	0.9(m,2H)	1.5(m,10H) 1.9(m,2H)		2.8(т,2H)	—	—	—	7.2(d,2H)	7.7(m,6H)
IIIa	0.2(s,6H)	0.3(d,6H)	0.8(m,2H)	1.5(m,10H) 1.9(m,2H)		2.8(т,2H)	4.9(m,1H)	—	—	7.2(d,2H)	7.7(m,6H)
IVa	0.1(s,12H)	0.2(s,96H)	0.8(m,64H)	1.5(m,124H) 1.9(m,16H)		2.8(т,16H)	—	—	—	7.2(d,16H)	7.7(m,48H)
Ib	—	—	—	1.5(m,10H) 1.9(m,2H)	2.2(m,2H)	2.8(т,2H)	—	5.2(d,2H)	6.0(m,1H)	7.1(d,2H)	7.4(d,2H)
IIb	—	0.4(s,6H)	0.9(m,2H)	1.5(m,10H) 1.9(m,2H)		2.8(т,2H)	—	—	—	7.1(d,2H) 7.3(d,2H)	7.4(d,2H) 8.4(d,2H)
IIIb	0.2(s,6H)	0.3(d,6H)	0.8(m,2H)	1.5(m,10H) 1.9(m,2H)		2.8(т,2H)	4.9(m,1H)	—	—	7.1(d,2H) 7.3(d,2H)	7.4(d,2H) 8.4(d,2H)
IVb	0.1(s,12H)	0.2(s,96H)	0.8(m,64H)	1.5(m,124H) 1.9(m,16H)		2.8(т,16H)	—	—	—	7.1(d,16H) 7.3(d,16H)	7.4(d,16H) 8.4(d,16H)
Ic	—	—	—				—	5.2(d,2H)	6.0(m,1H)		
IIc	—	0.4(s,6H)	0.9(m,2H)				—	—	—		
IIIc	0.2(s,6H)	0.3(d,6H)	0.8(m,2H)				4.9(m,1H)	—	—		
IVc	0.1(s,12H)	0.2(s,96H)	0.8(m,64H)				—	—	—		
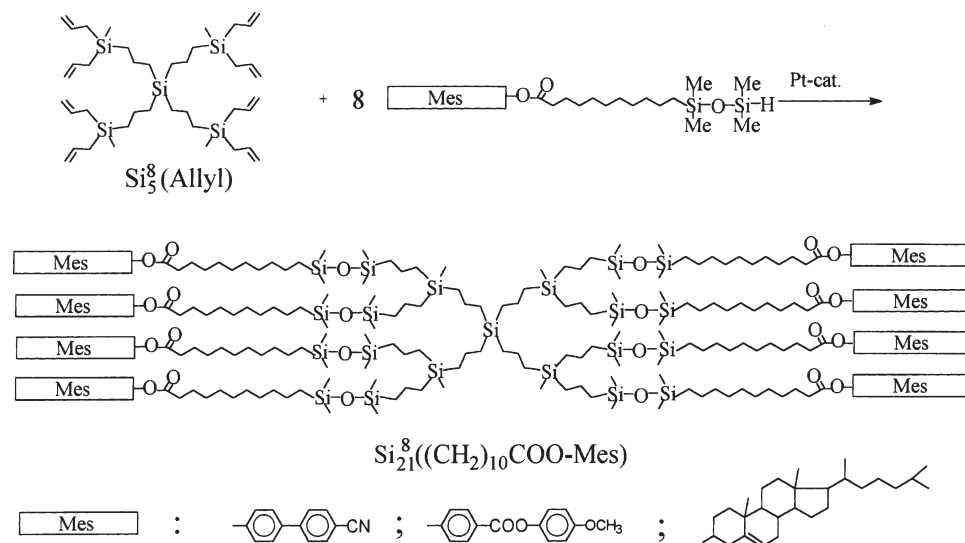
Figure 4.   Scheme of coupling of mesogen-containing fragments to the carbosilane dendritic matrix.

Pt-catalyst (figure 4). A l.5-fold excess of the mesogen-containing silane was used to guarantee bonding of mesogenic groups to all eight allyl groups of the dendritic matrix. After completion of the reaction, the excess of the former reactant was removed by column chromatography on silica gel. The final purification of the LC dendrimers was also carried out by chromatography.

The bands corresponding to the allylic double bonds of the initial dendritic matrix, $Si_8^5(Allyl)$, are absent both in the IR and Raman spectra of the final compounds **IVa**, **IVb** and **IVc**. The proton signals due to terminal carbon–carbon double bonds (doublet $\delta_1 = 5.2$ ppm and multiplet $\delta_2 = 6.0$ ppm) are absent in the PMR spectra of the same compounds. These facts prove the completeness of the final reaction. The structure of all LC dendrimers obtained was established by ^{1}H and ^{29}Si NMR spectroscopy. The ratio of the integral intensities of the signals due to protons of methyl groups at the different silicon atoms (singlet $\delta = 0.1$ ppm and $\delta = 0.2$ ppm) is close to the calculated value of 1:8. Data from PMR spectroscopy are represented in table 2.

The ^{29}Si NMR spectra of the compounds synthesized, $Si_{21}^8((CH_2)_{10}COO-Mes)$, are completely resolved: $\delta_1 = 0.75$ ppm, $\delta_2 = 1.28$ ppm, $\delta_3 = 6.74$ ppm, $\delta_4 = 7.29$ ppm. The ratio of the integral intensities of the signals due to the [29]Si nuclei corresponds to the calculated value: Si(1):Si(2):Si(3):Si(4)=1:4:8:8 (figure 5).

The purity of the final compounds obtained was established by GPC (table 3). For instance, the GPC trace of the LC dendrimer with cyanobiphenylyl mesogenic groups (figure 6) has a symmetric peak after final chromatographic purification. The molecular mass

distributions of the LC dendrimers obtained were within the limits of $1.01 \div 1.06$, confirming the monodispersity of LC dendrimers synthesized.

2.2.   Phase behaviour and structure of the LC dendrimers

The LC properties of the dendrimers obtained were determined by optical polarizing microscopy in combination with differential scanning calorimetry (DSC) measurements and X-ray diffraction. The transition temperatures of the compounds are listed in table 4. As can be seen from these data, the phase behaviour of the compounds under investigation generally depends on the chemical nature of the terminal mesogenic groups. This fact is in agreement with the idea mentioned above
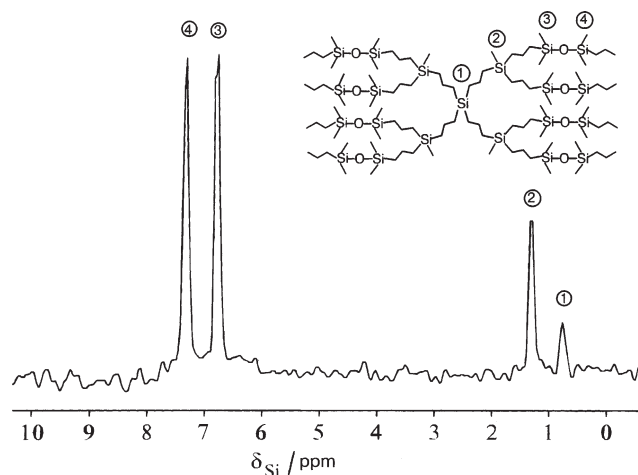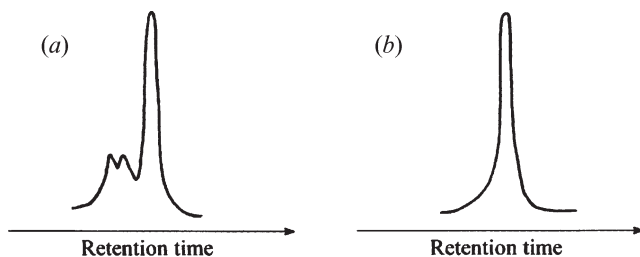

Figure 5.   ^{29}Si NMR spectrum of LC dendrimer $Si_{21}^8[(CH_2)_{10}COO-MPhB]$.

Table 3. Molecular mass characteristics of LC dendrimers.

LC dendrimer	M calculated/g mol^{-1}	M_n (GPC data)	M_w/M_n
$Si_{21}^8[(CH_2)_{10}COO-CB]$	4664	4280	1·01
$Si_{21}^8[(CH_2)_{10}COO-MPhB]$	5048	4352	1·06

Figure 6. GPC chromatogram of LC dendrimer $Si_{21}^8[(CH_2)_{10}COO-CB]$ (*a*) before and (*b*) after purification.

that many of the properties of dendrimers are determined mainly by the chemical nature of the terminal (surface) groups [4]. Let us consider the phase behaviour of each dendrimer synthesized.

The DSC thermogram of the *cholesteryl-containing dendrimer* (**IVc**) has one endothermic transition at $\sim100°C$ which corresponds to an enthalpy of $\Delta H=5.4\,J\,g^{-1}$ (figure 7, curve 1). Such a value of the enthalpy is characteristic of a smectic-isotropic transition. A second order phase transition corresponds to the glass transition temperature that is below room temperature ($T_g=-15°C$). According to polarizing microscopy, this compound is characterized by a focal-conic fan-shaped texture over the entire temperature range until the clearing point at $100°C$, figure 8 (*a*).

To determine the type of molecuar packing of the cholesteryl mesogenic groups, an X-ray diffraction study of the LC dendrimer was made at room temperature. The X-ray diffraction pattern of the unoriented sample

of **IVc** exhibits a diffuse halo at wide angles and two small angle reflections, figure 9 (*a*). These data and the results of the polarizing microscopy investigations allow us to conclude that the dendrimer **IVc** displays the smectic A mesophase. The diffuse halo D at $6.0\,\text{Å}$ (table 5) corresponds to the lateral spacing of two mesogenic terminal groups. This value is in agreement with the same distance for cholesteryl-containing combshaped polyacrylates and corresponds to the distance between the cholesteryl side groups. The sharp first order reflection at $45\,\text{Å}$, along with a second order reflection at $22\,\text{Å}$, corresponds to the smectic layer spacing.

The DSC heating curve of *cyanobiphenyl dendrimer* (**IVa**) contains one endothermic transition at $90°C$ which corresponds to an enthalpy of $\Delta H=5.1\,J\,g^{-1}$ (figure 7, curve 2). This enthalpy value falls in the typical range observed for smectic A to isotropic transitions. The second order phase transition at $-24°C$ corresponds to the glass transition temperature. The existence of two diffuse maxima at wide angles and two small angle reflections (the first and second orders) in the X-ray diffraction pattern of this compound over the entire temperature range up to the clearing point (figure 9 (*b*), table 5) confirms the smectic type of the mesophase.

On heating dendrimer **IVa** up to $50°C$ a coexistence of broken focal-conic and schlieren microscopic textures can be observed, figure 8 (*b*). The schlieren texture is transformed into a homeotropic texture at $50°C$, while the broken focal-conic texture remains unchanged,

Table 4. Phase transition temperatures of LC dendrimers.

LC dendrimer	Temperatures of phase transitions/°C
$Si_{21}^8[(CH_2)_{10}COO-Chol]$ (**IVc**)	g−15 S_A 100 I
$Si_{21}^8[(CH_2)_{10}COO-CB]$ (**IVa**)	g−24 S_C 50 S_A 90 I
$Si_{21}^8[(CH_2)_{10}COO-MPhB]$ (**IVb**)	Cr_1−4 Cr_2 27 S_C 76 I

Table 5. Interplanar spacings of LC dendrimers (Å).

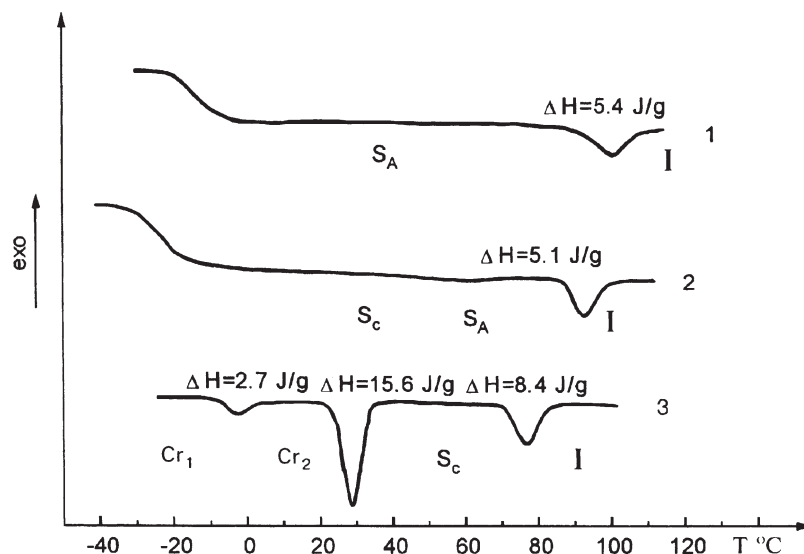| LC dendrimer	T/°C	$d_1\pm1$	$d_2\pm0.5$	$D\pm0.1$	$D_1\pm0.1$
$Si_{21}^8[(CH_2)_{10}COO-CB]$	60	43	22	5·0 dif.	6·5 dif.
$Si_{21}^8[(CH_2)_{10}COO-MPhB]$	50	42	21·5	5·5 dif.	7·1 dif.
$Si_{21}^8[(CH_2)_{10}COO-Chol]$	20	45	22	6·0 dif.	—

Figure 7.   DSC heating curves of LC dendrimers **IVc** (curve 1), **IVa** (curve 2) and **IVb** (curve 3).

figure 8 (*c*). These texture transitions can be explained in the following way. It is well known that the schlieren texture can be formed by the smectic tilted S_C mesophase. In this case the transition into the homeotropic texture can be ascribed to a $S_C \rightarrow S_A$ transition, because only orthogonal smectics can form a homeotropic texture. The absence of a peak at 50°C in the DSC curve is probably explained by the small heat of this transition. Thus, one can suppose that the LC dendrimer with cyanobiphenyl mesogenic groups displays the following phase transitions: $g \leftrightarrow S_C \leftrightarrow S_A \leftrightarrow I$.

The DSC thermogram of *methoxyphenyl benzoate dendrimer* (**IVb**) has three endothermic transitions at −4, 27 and 76°C (figure 7, curve 3). The transition at 27°C can be attributed to a crystal–smectic mesophase transition due to the large heat of this peak ($\Delta H = 15.6 \, \text{J g}^{-1}$). This is confirmed by X-ray diffraction. There are more than ten sharp reflections in the X-ray diffraction pattern at room temperature, while only two small angle reflections and two wide angle diffuse reflections are observed at 60°C (figure 9 (*b*), table 5). So the endotherm at 76°C ($\Delta H = 8.4 \, \text{J g}^{-1}$) can be ascribed to a disordered smectic–isotropic transition and the endotherm at −4°C ($\Delta H = 2.7 \, \text{J g}^{-1}$) to a crystal–crystal transition.

Polarizing microscopy data are in accordance with these conclusions. Dendrimer **IVb** displays fans of crystalline phase at room temperature, figure 8 (*d*). Heating up to 27°C destroys these fans and only a broken fanshaped texture characteristic of a tilted S_C mesophase is formed, figure 8 (*e*). The latter is not changed on heating up to the clearing point at 76°C. Hence, in all probability the LC dendrimer with

methoxyphenyl benzoate mesogenic groups is characterized by the phase transitions: $Cr_1 \leftrightarrow Cr_2 \leftrightarrow S_C \leftrightarrow I$.

It should be noted that there are two diffuse reflections in the X-ray diffraction patterns of both the cyanobiphenyl and methoxyphenyl benzoate LC dendrimers (figure 9 (*b*), table 5). One of them ($D = 5.0$–$5.5 \, \text{Å}$) corresponds to the distance between the mesogenic groups in the smectic layer. The other ($D = 6.5$–$7.1 \, \text{Å}$) can be ascribed to some ordering of the carbosilane matrix itself. However, the X-ray diffraction pattern for the cholesteryl LC dendrimer (figure 9 (*a*), table 5) contains only one wide angle diffuse reflection ($D = 6.0 \, \text{Å}$), corresponding to the distance between cholesteryl mesogenic groups in the smectic layer. This fact could be explained by a superposition of the two reflections described above. Detailed investigations concerning the structural peculiarities of the dendrimers synthesized are in progress.

3.   Experimental

3.1.   *Techniques*

The NMR spectra were recorded with a Bruker WP-200 spectrometer. In the case of ^{1}H NMR spectroscopy, 5 wt % solutions in CCl_4 were used, whereas in the case of ^{29}Si NMR spectroscopy, 40 wt % solutions in CCl_4 were utilized. The IR spectra were recorded with a Bruker IFS-88 spectrophotometer. Molecular mass characteristics were determined using THF solutions by GPC using a GPC-2 Waters liquid chromatograph equipped with an adsorption detector and three Ultrastyragel columns having pore sizes 100, 500 and 1000 Å. Chromatograms were processed using a Data
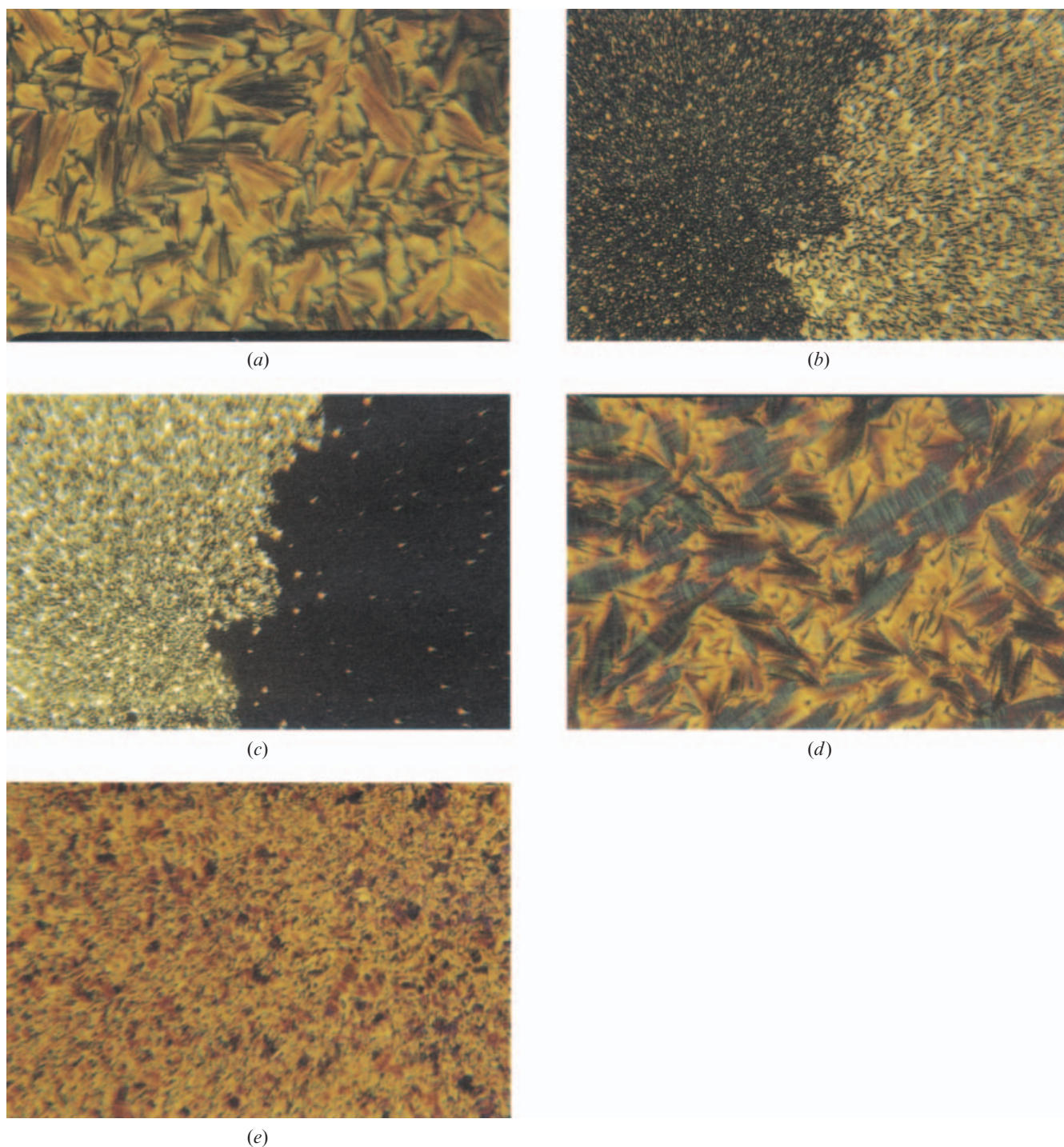
Figure 8. Optical polarizing photomicrographs: (*a*) fan-shaped texture of **IVc** (S$_A$, 20°C, magnification ×160); (*b*) coexistence of broken focal-conic and schlieren textures of **IVa** (S$_C$, 40°C, magnification ×64); (*c*) coexistence of broken focal-conic and homeotropic textures of **IVa** (S$_A$, 50°C, magnification ×64); (*d*) crystalline phase of **IVc** (Cr$_2$, 20°C, magnification ×160); (*e*) broken fan-shaped texture of **IVc** (S$_C$, 37°C, magnification ×64).

Modul-370 integrator. Silicagel 60 (0.063÷0.200) from Merck was used for column chromatography. Solvents were purified and dried according to standard procedures.

Transition temperatures were measured using a Mettler FP-800 central processor equipped with a Mettler FP-82 hot stage and control unit in conjunction with a Lomo R-112 polarizing microscope. DSC curves
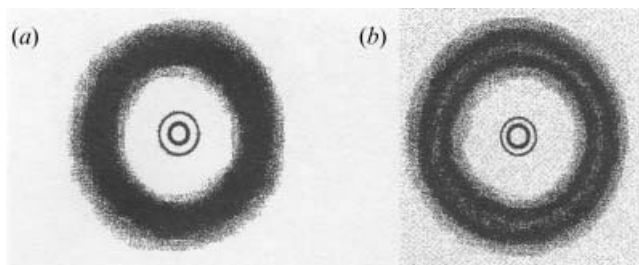
Figure 9. Schematic representation of X-ray diffraction patterns of (a) **IVc** (S_A mesophase, 20°C) and (b) **IVa** (S_C mesophase, 60°C).

were registered and calculated using the Mettler TA-4000 thermosystem. The heating rate was $10°C\,min^{-1}$. X-ray diffraction analysis was carried out using a URS-55 apparatus with Ni-filtered CuK_α-radiation ($\lambda = 1.542\,Å$).

3.2. Synthesis of LC dendrimer $Si_{21}^8 \left[(CH_2)_{10}COO-CB \right]$ (IVa)

3.2.1. 4′-Cyanobiphenyl-4-yl 10-undecenoate (Ia).
A solution of the acid chloride of 10-undecylenic acid ($5.57\,g$, $2.75 \times 10^{-2}\,mol$) in anhydrous THF ($25\,ml$) was added dropwise to a stirred, cooled (0°C) solution of 4-hydroxy-4′-cyanobiphenyl ($4.88\,g$, $2.5 \times 10^{-2}\,mol$) and triethylamine ($4.00\,m1$, $2.75 \times 10^{-2}\,mol$) in dry THF ($50\,ml$). The reaction mixture was stirred at room temperature for 24 h and then 150 ml of diethyl ether and 20 ml of water were added. The ether layer was washed with water, followed by a solution of sodium bicarbonate and, finally, with water again until the pH was neutral. After drying over magnesium sulphate, the ether was removed in vacuo ($1333\,Pa$). The residue was recrystallized three times from ethanol. Yield: $6.50\,g$ (72.0%). $T_{N-I}^\dagger = 71°C$ (lit. $T_{N-I} = 73°C$ [27]). PMR data are presented in table 2.

3.2.2. 4′-Cyanobiphen-4-yl 11-(dimethylchlorosilyl) undecanoate (IIa).
A mixture of compound **Ia** ($11.66\,g$, $3.23 \times 10^{-2}\,mol$), dimethylchlorosilane ($6.15\,g$, $6.5 \times 10^{-2}\,mol$) and a toluene solution of bis(N,N,N-trioctylbenzylamino) tetranitroplatinum ($0.1\,ml$, $6.5 \times 10^{-7}\,mol$) was heated in a closed vessel for 48 h at 95°C. The completion of the reaction was checked by the disappearance of the IR band in the region $1640\,cm^{-1}$, which is characteristic of the stretching vibration of the terminal C=C bond. After the reaction was complete, the toluene and excess of dimethylchlorosilane were

removed in vacuo ($1333\,Pa$) for 2 h. Yield: $14.4\,g$ (98%). PMR data are presented in table 2.

3.2.3. 4′-Cyanobiphen-4-yl 11-(tetramethyldisiloxy) undecanoate (IIIa).
A mixture of pyridine ($10.06\,ml$, $0.132\,mol$) and water ($2.4\,ml$, $0.132\,mol$) was added dropwise to an intensively stirred solution of compound **IIa** ($1.45\,g$, $3.2 \times 10^{-3}\,mol$) and dimethylchlorosilane ($12.06\,g$, $0,128\,mol$) in anhydrous THF ($35\,ml$). The reaction mixture was stirred for 2 h at 20°C. Then 100 ml of diethyl ether, 100 ml of pentane and 50 ml of water were added. The top layer was washed with water until the pH was neutral. After drying over magnesium sulphate the solvent was removed under reduced pressure ($1333\,Pa$). The residue was purified by column chromatography on silica gel using a toluene/ethyl acetate (10:1) mixture as eluent. Yield: $1.22\,g$ (77%). PMR data are presented in table 2.

3.2.4. LC dendrimer $Si_{21}^8 \left[(CH_2)_{10}COO-CB \right]$ (IVa).
A mixture of carbosilane dendritic matrix $Si[(CH_2)_3Si-(CH_3)(CH_2CH=CH_2)_2]_4$ ($0.193\,g$, $2.78 \times 10^{-4}\,mol$), compound **IIIa** ($1.60\,g$, $3.32 \times 10^{-3}\,mol$) and a toluene solution of bis(N,N,N-trioctylbenzylamino) tetranitroplatinum ($0.03\,ml$, $1.95 \times 10^{-7}\,mol$) was heated in a closed vessel for 48 h at 100°C. After evaporating in vacuo ($133\,Pa$), the product was isolated from the excess of compound **IIIa** by column chromatography using toluene as eluent. Final chromatographic purification was carried out using a toluene/ethyl acetate (10:1) mixture as eluent. Yield: $1.15\,g$ (90%). PMR data are presented in table 2. Found: C, 67.95; H, 8.63; Si, 12.53; N, 2.45%. Calcd for $Si_{21}^8 \left[(CH_2)_{10}COO-CB \right]$ (**IVa**): C, 67.99; H, 8.73; Si, 12.65; N, 2.40%.

3.3. Synthesis of LC dendrimer $Si_{21}^8 \left[(CH_2)_{10}COO-MPhB \right]$ (IVb)

3.3.1. 4-Methoxyphenyl 4′-(10-undecenoyloxy)benzoate (Ib).
The experimental procedure described for the preparation of compound **Ia** was used. 4-Methoxyphenyl 4′-hydroxybenzoate ($6.71\,g$, $2.75 \times 10^{-2}\,mol$), the acid chloride of 10-undecylenic acid ($5.07\,g$, $2.5 \times 10^{-2}\,mol$), triethylamine ($4.00\,ml$, $2.5 \times 10^{-2}\,mol$) and dry THF ($50\,ml$) were used. The crude product was purified by column chromatography using a toluene/ethyl acetate (20:1) mixture as eluent. Yield: $9.8\,g$ (87%). $T_{N-I} = 70°C$ (lit. $T_{N-I} = 74°C$ [27]). PMR data are presented in table 2.

3.3.2. 4′-Methoxyphenyl 4′-[11-(dimethylchlorosilyl) undecanoyloxy]benzoate (IIb).
This compound was synthesized from **Ib** ($10.0\,g$, $2.44 \times 10^{-2}\,mol$) and dimethylchlorosilane ($4.6\,g$, $4.88 \times 10^{-2}\,mol$) using the

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† T_{N-I} is the phase transition temperature: nematic mesophase-isotropic melt.

same procedure as for **IIa.** Yield: 12.0 g (98%). PMR data are presented in table 2.

3.3.3. 4-Methoxyphenyl 4′-[11-(tetramethyldisiloxy) undecanoyloxy]benzoate (IIIb).
The experimental procedure used was the same as that described for compound **IIIa.** Compound **IIb** (3.63 g, 7.55×10^{-3} mol), dimethylchlorosilane (14.2 g, 0.15 mol), pyridine (14.0 ml, 0.174 mol) and water (3.15 ml, 0.174 mol) were used. Yield: 1.47 g (36%). PMR data are presented in table 2.

3.3.4. LC dendrimer $Si_{21}^{8}\left[(CH_2)_{10}COO-MPhB\right]$ (IVb).
Compound **IVb** was synthesized from **IIIb** (1.85 g, 3.4×10^{-3} mol) and carbosilane dendritic matrix $Si[(CH_2)_3Si(CH_3)(CH_2CH=CH_2)_2]_4$ (0.198 g, 2.84×10^{-4} mol) using the procedure given for compound **IVa.** The crude product was purified by column chromatography using a toluene/ethyl acetate (10:1) mixture as eluent. Yield: 1.29 g (90%). PMR data are presented in table 2. Found: C, 64.62; H, 8.62; Si, 11.44%. Calcd for $Si_{21}^{8}\left[(CH_2)_{10}COO-MPhB\right]$ (**IVb**): C, 64.61; H, 8.53; Si, 11.66%.

3.4. Synthesis of LC dendrimer $Si_{21}^{8}\left[(CH_2)_{10}COO-Chol\right]$ (IVb)

3.4.1. Cholesteryl 10-undecenoate (Ic).
The experimental procedure described for the preparation of compound **Ia** was used. Cholesterol (10.0 g, 0.03 mol), the acid chloride of 10-undecylenic acid (7.93 g, 0.04 mol), triethylamine (6.00 ml, 0.04 mol) and dry THF (50 ml) were used. The crude product was purified by column chromatography using toluene as eluent. Yield: 9.0 g (61 %). $T_{\text{Chol-I}}{}^{\dagger}$=82°C (lit. $T_{\text{Chol-I}}$=81°C [26]). PMR data are presented in table 2.

3.4.2. Cholesteryl 11-(dimethylchlorosilyl)undecanoate (IIc).
This compound was synthesized from compound **Ic** (6.10 g, 0.011 mol) and dimethylchlorosilane (3.13 g, 0.033 mol) using the same procedure as for **IIa.** Yield: 6.86 g (96%). PMR data are presented in table 2.

3.4.3. Cholesteryl 11-(tetramethyldisiloxy)undecanoate (IIIc).
The experimental procedure used was the same as that described for **IIIa.** Compound **IIc** (3.5 g, 5.5×10^{-3} mol), dimethylchlorosilane (21 g, 0.22 mol), pyridine (18.2 ml, 0.23 mol) and water (4.1 ml, 0.23 mol) were used. Yield: 2.7 g (73%). PMR data are presented in table 2.

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† $T_{\text{Chol-I}}$ is the phase transition temperature: cholesteric mesophase–isotropic melt.

3.4.4. LC dendrimer $Si_{21}^{8}\left[(CH_2)_{10}COO-Chol\right]$ (IVc).
The compound **IVc** was synthesized from **IIIc** (2.63 g, 3.83×10^{-3} mol) and carbosilane dendritic matrix $Si[(CH_2)_3Si(CH_3)(CH_2CH=CH_2)_2]_4$ (0.170 g, 2.42×10^{-4} mol) using the procedure given for compound **IVa.** The crude product was purified by column chromatography using a toluene/ethyl acetate (10:1) mixture as eluent. Yield: 1.2 g (80%). PMR data are presented in table 2. Found: C, 72.90; H, 11.55; Si, 9.82%. Calcd for $Si_{21}^{8}\left[(CH_2)_{10}COO-Chol\right]$ (**IVc**): C, 72.91; H, 11.70; Si, 9.49%.

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