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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 ball-shaped 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 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-

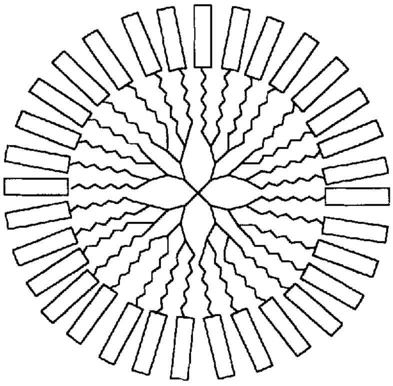

Figure 1. Schematic representation of the molecular structure of the LC dendrimer.

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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.

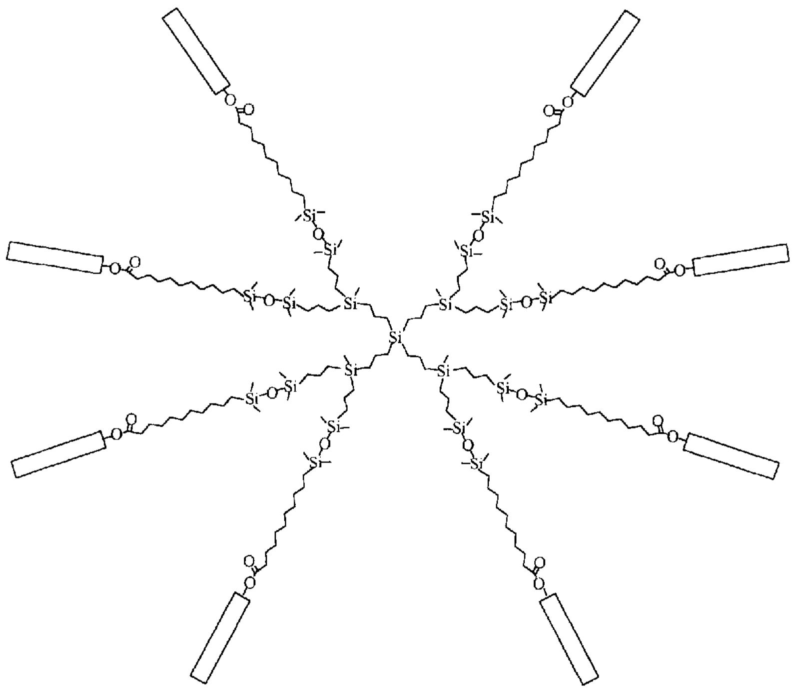
The possibility of the creation of an LC shell ('jacket') around a central nucleus, formed by the 'soft' dendritic matrix, is also interesting from the practical point of view. It opens up perspectives for the application of such compounds as active structural modifiers which can be introduced into usual 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.

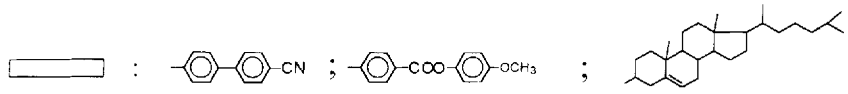
The second method, called usually the controlled synthesis, is based on the sequential assembly of individual molecular fragments using a layer-by-layer synthetic method via reiterative sequences of reactions of lower 'growth' with protection and deprotection of reactive groups. The merits of this method 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:



$\mathrm{Si}_{21}^{8}[(\mathrm{CH}_2)_{10}\mathrm{COO\text{-}Mes}]$



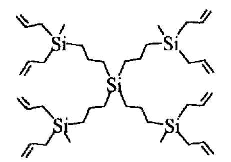
This paper presents a detailed description of the synthesis of the three different new dendrimers of the first generation†, containing only eight mesogenic groups, and our preliminary data on their structure and phase behaviour.

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_5^8(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.

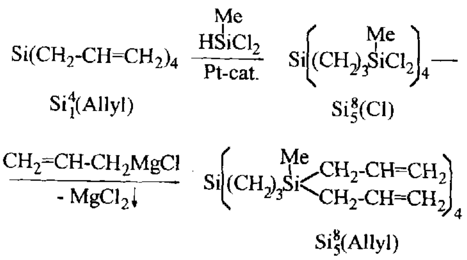
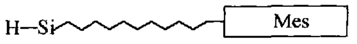


Figure 2. Scheme of synthesis of the dendritic matrix.

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-(dimethylchlorosilyl)undecanoic acid (compounds **IIa**, **IIb** and **IIc**) were obtained by the hydrosilylation of compounds **Ia**, **Ib** and **Ic** with

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† 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.

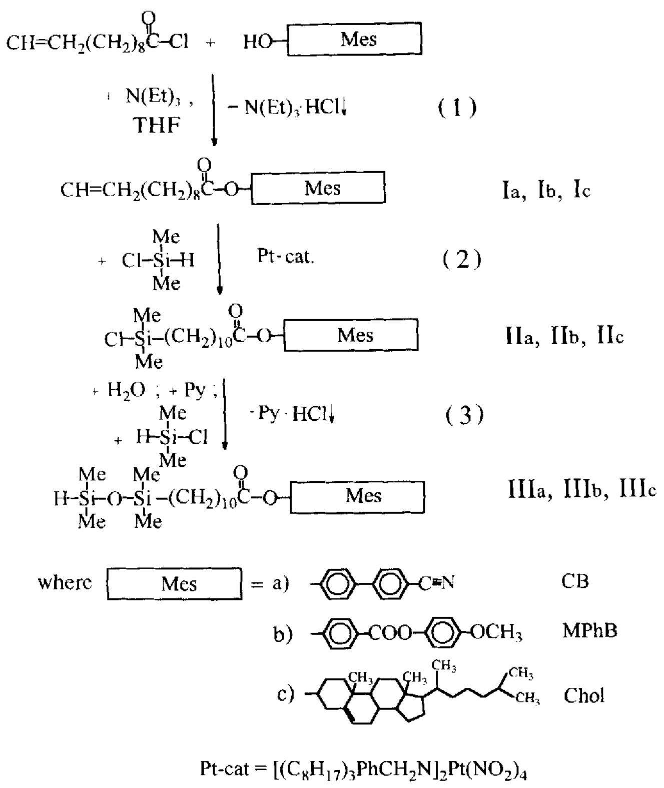


Figure 3. Scheme of synthesis of mesogen-containing fragments with reactive terminal groups.

dimethylchlorosilane in the absence of solvent. Bis(*N*,*N*,*N*-trioctylbenzylamino)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–CH$_3$ 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 $\delta_1 = 5{\cdot}2$ ppm and multiplet at $\delta_2 = 6{\cdot}0$ 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 × 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

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, T is triplet, m is multiplet. Here and in the text the figure before H is the number of hydrogen atoms.

	Chemical shifts δ/ppm.										
Compound	$Si–CH_3$		$Si–CH_2$–	–CH_2–			Si–H	CH_2=CH–		Ar–H	
Ia	—	—	—	1·5(m,10H) 1·9(m,2H)	2·2(m,2H)	2·8(T,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(T,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(T,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(T,16H)	—	—	—	7·2(d,16H)	7·7(m,48H)
Ib	—	—	—	1·5(m,10H) 1·9(m,2H)	2·2(m,2H)	2·8(T,2H)	—	5·2(d,2H)	6·0(m,1H)	7·1(d,2H) 7·3(d,2H)	7·4(d,2H) 8·4(d,2H)
IIb	—	0·4(s,6H)	0·9(m,2H)	1·5(m,10H) 1·9(m,2H)	—	2·8(T,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(T,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(T,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)				—	—	—		

out by hydrosilylation in the presence of Pt-catalyst (figure 4). A 1·5-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$^5_8$(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 $\delta_1 = 5{\cdot}2$ ppm and multiplet $\delta_2 = 6{\cdot}0$ 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 $\delta = 0{\cdot}1$ ppm and $\delta = 0{\cdot}2$ 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$^8_{21}$((CH$_2$)$_{10}$COO–Mes), are completely resolved: $\delta_1 = 0{\cdot}75$ ppm, $\delta_2 = 1{\cdot}28$ ppm, $\delta_3 = 6{\cdot}74$ ppm, $\delta_4 = 7{\cdot}29$ 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

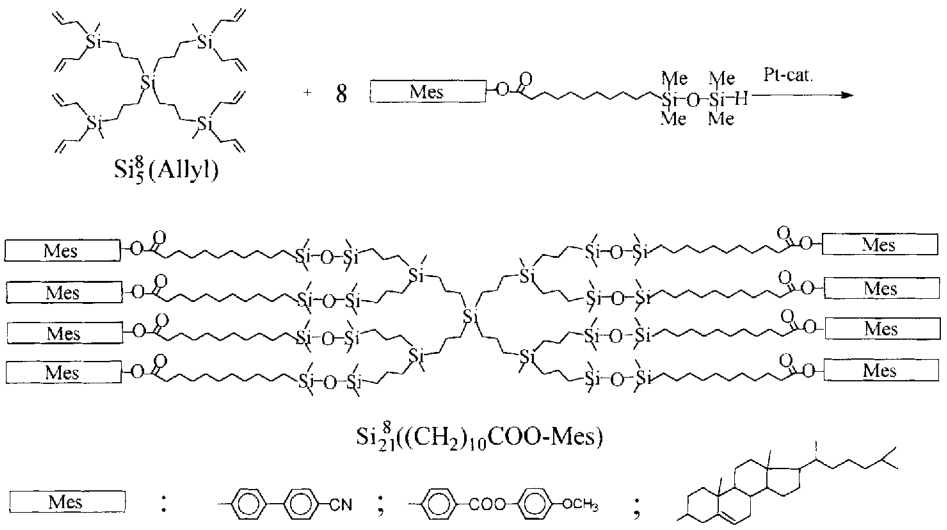


Figure 4. Scheme of coupling of mesogen-containing fragments to the carbosilane dendritic matrix.

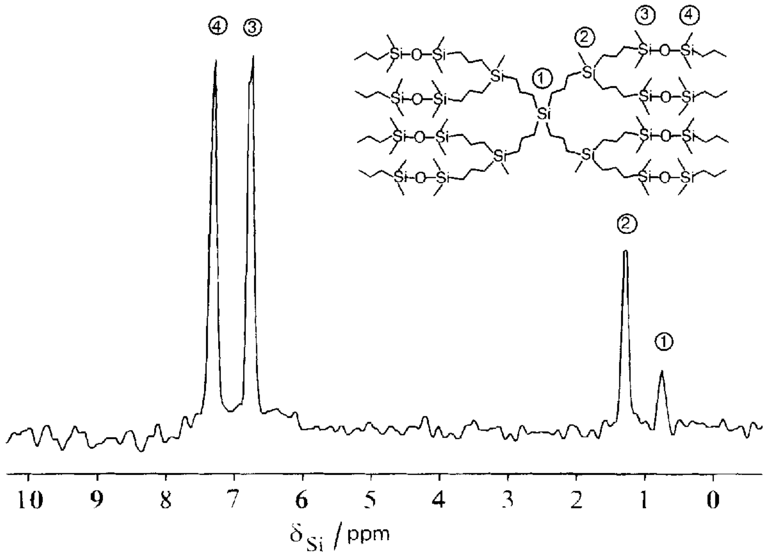


Figure 5. ^{29}Si NMR spectrum of LC dendrimer Si$^8_{21}$[(CH$_2$)$_{10}$COO–MPhB].

Table 3. Molecular mass characteristics of LC dendrimers.

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

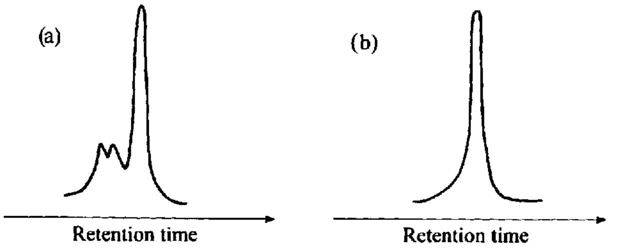


Figure 6. GPC chromatogram of LC dendrimer $Si_{21}^{8}[(CH_2)_{10}COO\text{-}CB]$ (*a*) before and (*b*) after purification.

the limits of 1·01 ÷ 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 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 ~100°C which corresponds to an enthalpy of $\Delta H = 5{\cdot}4\,\mathrm{J\,g^{-1}}$ (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 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 comb-shaped polyacrylates and corresponds to the distance between the cholesteryl side groups. The sharp first order reflection at 45 Å, along with a second order reflection at 22 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 $\Delta H = 5{\cdot}1\,\mathrm{J\,g^{-1}}$ (figure 7, curve 2). This enthalpy value falls in the typical range

Table 4. Phase transition temperatures of LC dendrimers.

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

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

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

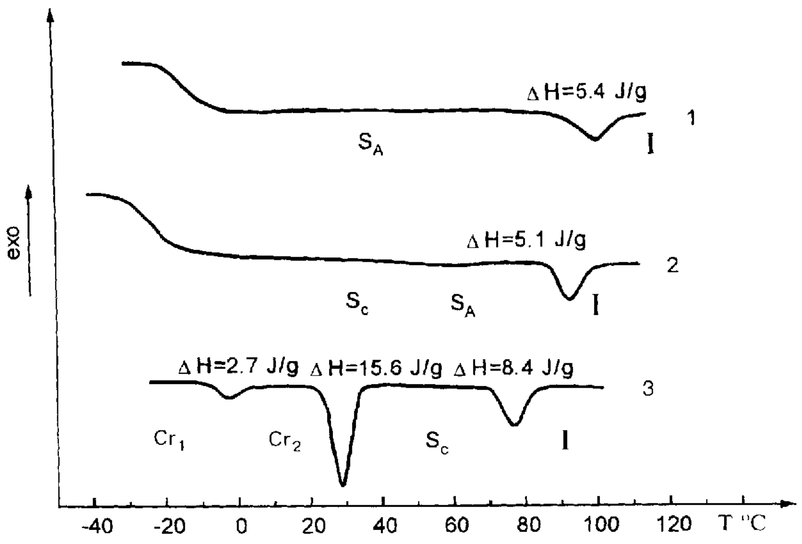


Figure 7. DSC heating curves of LC dendrimers **IVc** (curve 1), **IVa** (curve 2) and **IVb** (curve 3).

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, 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 ($\Delta H = 15{\cdot}6\,\mathrm{J\,g^{-1}}$). 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 ($\Delta H = 8{\cdot}4\,\mathrm{J\,g^{-1}}$) can be ascribed to a disordered smectic–isotropic transition and the endotherm at -4°C ($\Delta H = 2{\cdot}7\,\mathrm{J\,g^{-1}}$) to a crystal–crystal transition.

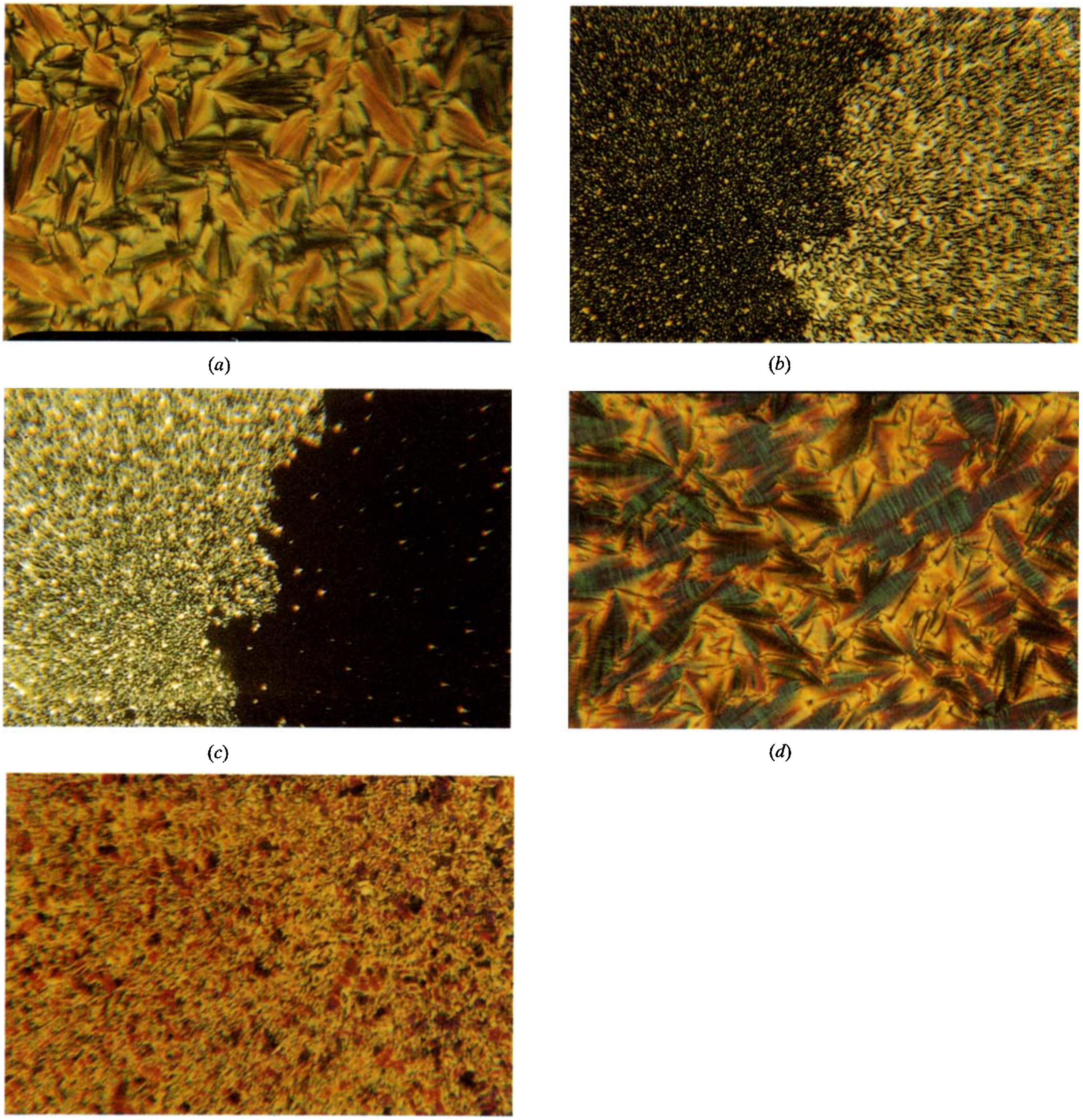
Polarizing microscopy data are in accordance with these conclusions. Dendrimer **IVb** displays fans of crystalline phase at room temperature, figure 8 (*d*). Heating up to 27°C destroys these fans and only a broken fan-shaped texture characteristic of a tilted S_C mesophase is formed, figure 8 (*e*). 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 ($D = 5{\cdot}0 \div 5{\cdot}5$ Å) corresponds to the distance between the mesogenic groups in the smectic layer. The other ($D = 6{\cdot}5 \div 7{\cdot}1$ 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 ($D = 6{\cdot}0$ 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 pecularities 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



(*a*) (*b*)

(*c*) (*d*)

(*e*)

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).

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

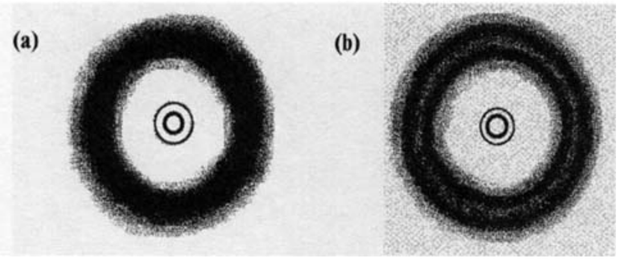


Figure 9. Schematic representation of X-ray diffraction patterns of (*a*) **IVc** (S_A mesophase, 20°C) and (*b*) **IVa** (S_C mesophase, 60°C).

Ultrastyragel columns having pore sizes 100, 500 and 1000 Å. Chromatograms were processed using a Data 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 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$_\alpha$-radiation ($\lambda = 1{\cdot}542$ Å).

3.2. *Synthesis of LC dendrimer* $Si_{21}^{8}[(CH_2)_{10}COO\text{–}CB]$ (**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 × 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 × 10^{-2} mol) and triethylamine (4·00 ml, 2·75 × 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%). $T_{N\text{–}I}$† = 71°C (lit. $T_{N\text{–}I}$ = 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 × 10^{-2} mol), dimethylchlorosilane (6·15 g, 6·5 × 10^{-2} mol) and a toluene solution of bis(*N*,*N*,*N*-trioctylbenzylamino)tetranitroplatinum (0·1 ml, 6·5 × 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 × 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* $Si_{21}^{8}[(CH_2)_{10}COO\text{–}CB]$ (**IVa**)

A mixture of carbosilane dendritic matrix $Si[(CH_2)_3Si(CH_3)(CH_2CH{=}CH_2)_2]_4$ (0·193 g, 2·78 × 10^{-4} mol), compound **IIIa** (1·60 g, 3·32 × 10^{-3} mol) and a toluene solution of bis(*N*,*N*,*N*-trioctylbenzylamino)tetranitroplatinum (0·03 ml, 1·95 × 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 $Si_{21}^{8}[(CH_2)_{10}COO\text{–}CB]$ (**IVa**): C, 67·99; H, 8·73; Si, 12·65; N, 2·40%.

3.3. *Synthesis of LC dendrimer* $Si_{21}^{8}[(CH_2)_{10}COO\text{–}MPhB]$ (**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 × 10^{-2} mol), the acid chloride of 10-undecylenic acid (5·07 g, 2·5 × 10^{-2} mol), triethylamine (4·00 ml, 2·5 × 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%). $T_{N\text{–}I}$ = 70°C

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† $T_{N\text{–}I}$ is the phase transition temperature: nematic mesophase–isotropic melt.

(lit. $T_{N\text{-}I} = 74°C$ [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, $2{\cdot}44 \times 10^{-2}$ mol) and dimethylchlorosilane (4·6 g, $4{\cdot}88 \times 10^{-2}$ mol) using the 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, $7{\cdot}55 \times 10^{-3}$ 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* $Si_{21}^{8}[(CH_2)_{10}COO\text{–}MPhB]$ (**IVb**)

Compound **IVb** was synthesized from **IIIb** (1·85 g, $3{\cdot}4 \times 10^{-3}$ mol) and carbosilane dendritic matrix $Si[(CH_2)_3Si(CH_3)(CH_2CH{=}CH_2)_2]_4$ (0·198 g, $2{\cdot}84 \times 10^{-4}$ 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 $Si_{21}^{8}[(CH_2)_{10}COO\text{–}MPhB]$ (**IVb**): C, 64·61; H, 8·53; Si, 11·66%.

3.4. *Synthesis of LC dendrimer* $Si_{21}^{8}[(CH_2)_{10}COO\text{–}Chol]$ (**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%). $T_{Chol\text{-}I}$† = 82°C (lit. $T_{Chol\text{-}I}$ = 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, $5{\cdot}5 \times 10^{-3}$ 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.

3.4.4. *LC dendrimer* $Si_{21}^{8}[(CH_2)_{10}COO\text{–}Chol]$ (**IVc**)

The compound **IVc** was synthesized from **IIIc** (2·63 g, $3{\cdot}83 \times 10^{-3}$ mol) and carbosilane dendritic matrix $Si[(CH_2)_3Si(CH_3)(CH_2CH{=}CH_2)_2]_4$ (0·170 g, $2{\cdot}42 \times 10^{-4}$ 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 $Si_{21}^{8}[(CH_2)_{10}COO\text{–}Chol]$ (**IVc**): C, 72·91; H, 11·70; Si, 9·49%.

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

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