Synthesis and characterization of liquid crystalline monofunctionalized 'two chain' diols and corresponding low molecular weight siloxane derivatives

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Synthesis and characterization of liquid crystalline monofunctionalized 'two chain' diols and corresponding low molecular weight siloxane derivatives

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The selective synthesis and the thermal behaviour of some *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-(alkenyloxy, alkyloxy)benzoates (monofunctionalized 'two chain' diols) are described. Thus, several 3-(alkyloxy)-4-(undecenyloxy)benzoic acids and 4-(decyloxy)-3-(undecenyloxy)benzoic acid have been obtained. The monofunctionalized 'two chain' diols form a hexagonal columnar mesophase through hydrogen bonding. Subsequently, low molecular weight liquid crystalline siloxanes, model compounds for polymers, i.e. two twins and one cyclic product, were synthesized via a hydrosilylation reaction. With respect to the 'two chain' diols, the observed hexagonal columnar mesophase was stabilized and the intercolumnar distance was extended by the siloxane moieties. Remarkably, the thermal behaviour of the cyclosiloxane differs from that of the twins. A cubic mesophase, which can be observed very rarely in thermotropic mesogens, was formed at temperatures below the hexagonal columnar phase.

1. Introduction

3,4-Bis(alkoxy)benzoate groups often lead to highly stable mesophases or an interesting polymorphism in different classes of liquid crystal materials such as biforked mesogens [1], azamacrocyclic derivatives [2, 3] or diol mesogens [4, 5].

Cis,cis-(3,5-dihydroxycyclohexyl) 3,4,5-tris(alkyloxy)benzoates, 'three chain' diols, have been shown to be a new class of liquid crystalline compounds, where intermolecular interactions, i.e. hydrogen bonding, play a dominant role in the formation of hexagonal columnar mesophases [6–9]. The synthesis of a corresponding monofunctionalized 'three chain' diol and its polymer-analogous reaction to yield the relevant liquid crystalline polysiloxanes have been described [10]. Furthermore, investigations of *cis,cis*-(3,5-dihydroxycyclohexyl) 3,4-bis(alkyloxy)benzoates, 'two chain' diols, have shown that they undergo mesophase transitions with little dependent on the length of the alkoxy chains [4, 5]. The type of mesophase can change from a lamellar to a hexagonal columnar structure via an intermediate cubic mesophase [4].

In order to obtain liquid crystalline side chain polymers with a 'two chain' diol unit, it was necessary to find a selective synthesis for a monofunctionalized 'two chain' diol, i.e. 3-(alkyloxy)-4-(undecenyloxy)benzoic acid or isomers thereof.

In this paper, we want to describe the synthesis, characterization and mesophase behaviour of some monofunctionalized 'two chain' diols and related low molecular siloxanes, model compounds for polymers. All products have been dried prior to characterization.
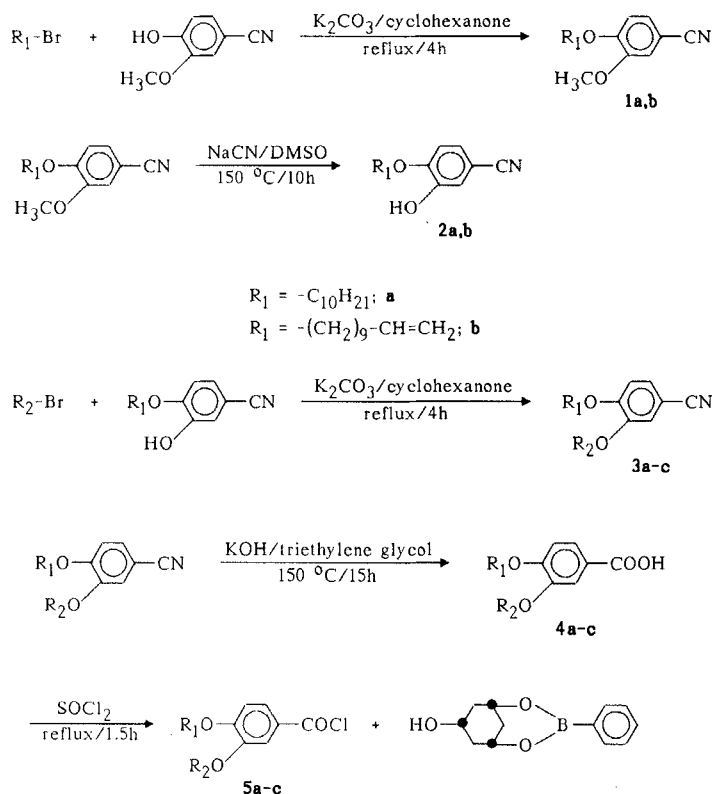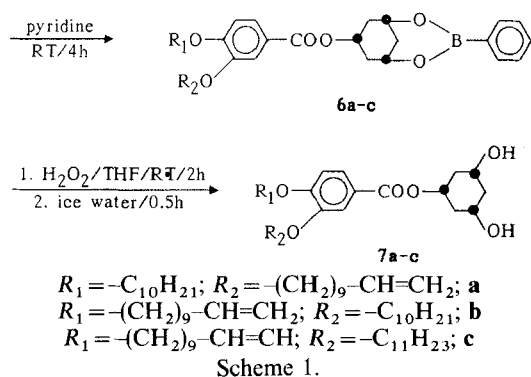
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2. Synthesis

The synthesis of the 3,4-(alkyloxy, undecenyloxy)benzoic acids (**4a–c**; scheme 1) was successfully achieved using a methyl aryl ether function as the protecting group.

Etherification of 4-hydroxy-3-methoxybenzonitrile (vanillic acid nitrile) with undenecyl- or alkyl bromide led to the derivatives **1a, b** (scheme 1). According to the literature [11, 12], the methyl aryl ether function could be cleaved selectively in the presence of an alkyl aryl- or undecenyl aryl ether group with sodium cyanide in dimethylsulphoxide (DMSO) as a nucleophilic reagent. The experimental conditions allowed us to obtain the pure phenols **2a, b** in high yields. The quantitative cleavage of the methyl aryl ether group was checked by ^{1}H NMR. Instead of the singlet of the methoxy group at 3·87 ppm in **1b**, in **2b** a phenolic proton appears at 5·76 ppm. Furthermore, a low field shift of the aromatic proton near the hydroxy group, from 7·05 to 7·15 ppm is detectable. The detailed spectroscopic data are given in the experimental part.

A second etherification step yielded the 3,4-(alkyloxy, undecenyloxy)benzonitriles **3a–c**. Saponification of the nitrile led to the desired benzoic acids **4a–c**, which could be purified by recrystallization.

Subsequent reaction steps, like formation of the acid chlorides **5a–c**, esterification with 3-phenyl-2,4-dioxa-3-bora-bicyclo[3.3.1]-nonan-7-ol, and deprotection of the compounds **6a–c**, were carried out under well-known conditions [6, 10] to yield the monofunctionalized 'two chain' diols **7a–c**. All the diols could be purified by column chromatography.

$$\xrightarrow[\text{RT/4h}]{\text{pyridine}}$$

6a-c

$$\xrightarrow[\text{2. ice water/0.5h}]{\text{1. H}_2\text{O}_2/\text{THF/RT/2h}}$$

7a-c

$R_1 = -C_{10}H_{21};\ R_2 = -(CH_2)_9-CH=CH_2;\ \textbf{a}$
$R_1 = -(CH_2)_9-CH=CH_2;\ R_2 = -C_{10}H_{21};\ \textbf{b}$
$R_1 = -(CH_2)_9-CH=CH;\ R_2 = -C_{11}H_{23};\ \textbf{c}$

Scheme 1.

For the hydrosilylation reaction it is necessary to use compound **6** pure. Purification by column chromatography was impossible, because phenylboric acid derivatives undergo fast decomposition in acidic media or on silica gel. Therefore it seemed to be better to reconvert the purified diol **7c** to the monomer **6c** by protecting it again with phenylboric acid in dioxan (scheme 2). Small amounts of polar impurities

7c

$$\xrightarrow[\text{- 2 H}_2\text{O}]{\text{dioxan}}$$

6c

+

n = 1; **8a**
n ≈ 5; **8b**

9

1. catalyst/toluene/RT/24h
2. H$_2$O$_2$/THF/RT/5h
3. ice water/2h

n = 1; **10a**
n ≈ 5; **10b**

11

$R = -(CH_2)_{11}O$⟨⟩$-COO$...OH / $H_3C(CH_2)_{10}O$ ...OH
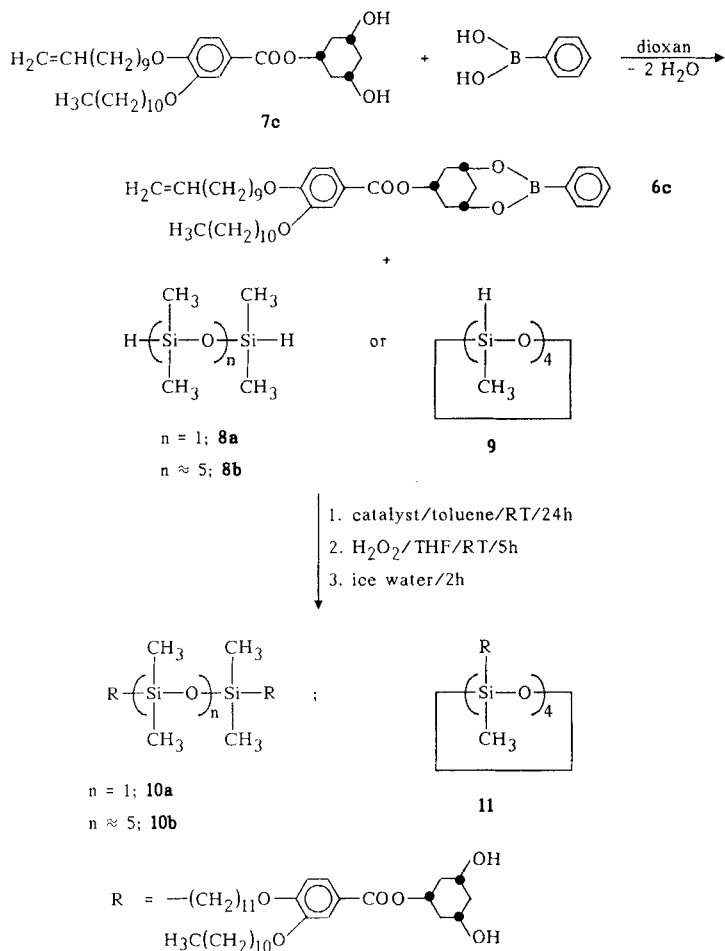
Scheme 2.

still existing in the 'reprotected' compound **6c** could now be removed by precipitation in hexane. All physical data for **6c** confirm the structure and are summarized in the experimental part.

The syntheses of the low molecular weight siloxane model compounds were carried out according to scheme 2 by a hydrosilylation reaction of **6c** with different H-siloxanes **8a, b** and **9**, using a platinum catalyst. Without preceding purification, the resulting phenylboric acid derivatives were deprotected. In this way, two different siloxane twins **10a, b** and one cyclic siloxane model compound **11** were obtained in good yields. All new compounds, except the acid chlorides **5a–c** and the phenylboric acid derivatives **6a, b**, were characterized by IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry (MS) and elemental analysis. SEC and TLC were used to check the purity. All the data, summarized in the experimental part, confirm the structures.

3. Phase behaviour

Like the 3,4,5-tris(alkoxy)benzoic acids [13], the 'two chain' benzoic acids **4a–c** do not exhibit mesomorphism. The liquid crystalline behaviour of the diols **7a–c** and the siloxane compounds **10a, b** and **11** was investigated by differential scanning calorimetry (DSC) and polarizing microscopy, as well as by X-ray measurements. In order to obtain reproducible transition temperatures, **7a–c** were freeze dried from a benzene solution. All the DSC data from second heating curves are summarized in table 1.

The monofunctionalized 'two chain' diols **7a–c** have a nearly identically thermal behaviour. By variation of the position (*para*- or *meta*-) and the length of the side chains (decyloxy or undecenyloxy), only a small shift in the transition temperatures is detectable. Therefore the second heating and cooling curve of **7c** shown in figure 1 is representative.

Table 1. Thermal data for compounds **7a–c** from second heating curves (heating rate $10°C \, min^{-1}$). Transition temperatures (°C) and, in brackets, transition enthalpies (kJ mol^{-1}). (T_g = glass transition temperature; C = crystalline phase; M_1 = mesophase 1; M_2 = mesophase 2; I = isotropic melt.)

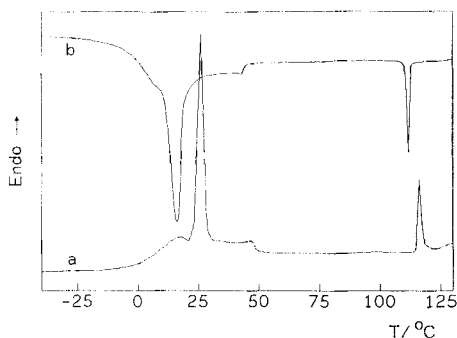| Compound	T_g	C		M_1		M_2		I
7a	7	●	17·5 (7·3)	●	44	●	112·5 (1·1)	●
7b	8	●	19 (7·6)	●	42	●	110 (1·1)	●
7c	7	●	25·5 (8·3)	●	47	●	115 (1·2)	●

Figure 1. DSC thermogram of the monofunctionalized 'two chain' diol **7c** (heating and cooling rate $10°C \, min^{-1}$). (*a*) Second heating curve; (*b*) cooling curve.

The weak endothermic peak at 115°C ($\Delta H = 1\cdot2\,\mathrm{kJ\,mol^{-1}}$) in the heating curve of **7c** is for a transition from a mesophase M_2 into the isotropic phase. In comparison to the unfunctionalized 'two chain' diol with eleven C-atoms in the side chain with a clearing temperature $T_c = 123°C$ [5], compound **7c** exhibits a lower T_c. This effect illustrates the destabilizing influence of a terminal double bond in one side chain [10]. A stronger endothermic peak, the melting peak at $T_m = 25\cdot5°C$ ($\Delta H = 8\cdot3\,\mathrm{kJ\,mol^{-1}}$) marks the transition from the crystalline phase C into a mesophase M_1. At 47°C, a transition from M_1 to M_2 can be observed as a step in the thermogram. This transition is also detectable in the cooling curve at 44°C. Furthermore a glass transition (T_g) can be observed in the heating curve at 7°C.

The clearing temperatures of the isomeric diols **7a** and **7b** differ by 2·5°C. This indicates a slightly larger destabilizing effect of a terminal double bond in the *para-* than in the *meta*-position of the aromatic core. Representatively for all compounds **7**, the pseudo-focal-conic texture of M_2 for **7c**, observed by the polarizing microscopy, is given in figure 2 (*a*). The pseudo-focal-conic or spherolithic texture is the same as for the unfunctionalized 'two chain' diols with more than ten C-atoms in the side chain, possessing a hexagonal columnar mesophase. In the range of the mesophase M_1, the texture changes to pseudo-focal-conics with concentric arcs (see figure 2 (*b*)). Such a phenomenon was described earlier for a liquid crystalline azacyclic derivative containing a 3,4-bis(decyloxy)benzoyl substituent [3]. Preliminary X-ray measurements show the presence of mesophase M_1 in the temperature range between 25·5 and 47°C. The determination of the phase type is still under investigation. By analogy with the unfunctionalized 'two chain' diols with more than ten C-atoms in the side chain [5], X-ray measurements at temperatures above 50°C reveal the hexagonal columnar disordered structure of the mesophase M_2 with lattice constants between 40·0 and 43·0 Å, as shown in table 2. As expected, compound **7c** with the longer unfunctionalized alkoxy side chain exhibits the largest intercolumnar distance of 43 Å. The non-discoid single diols form a columnar mesophase by aggregation of the 1,3-cyclohexane diol head groups via hydrogen bonding.

All the siloxane model compounds **10a, b** and **11** are insoluble in benzene. Therefore, instead of freeze drying, all products were dried in a vacuum shelf drier at 95°C, in the presence of phosphorus pentaoxide, over a period of 36 h.

By means of DSC and polarizing microscopy, the data in table 3 were established. Sequences of transition temperatures similar to those for the compounds **7** (table 1), are detectable at generally higher temperatures for the corresponding siloxane twins **10a, b**. As can be seen from the thermograms (see figures 3 (*a*), (*b*)), the unusual mesophase M_1 appears on heating, with a step at 57 or 69°C, respectively. M_1 can be frozen in below room temperature, because no crystalline state is detectable.

Table 2. X-ray data for the hexagonal columnar mesophases of compounds **7a–c**. (T = measuring temperature; d_{hkl} = lattice spacings; a_{hex} = lattice constant calculated from d_{200} value.)

Compound	$T/°C$	$d_{hkl}/\text{Å}$			Halo/Å	$a_{hex}/\text{Å}$
		100	110	200		
7a	90	33·9	20·4	17·6	4·55	40·6
7b	90	33·1	19·9	17·3	4·55	40·0
7c	70	35·8	21·5	18·6	4·50	43·0
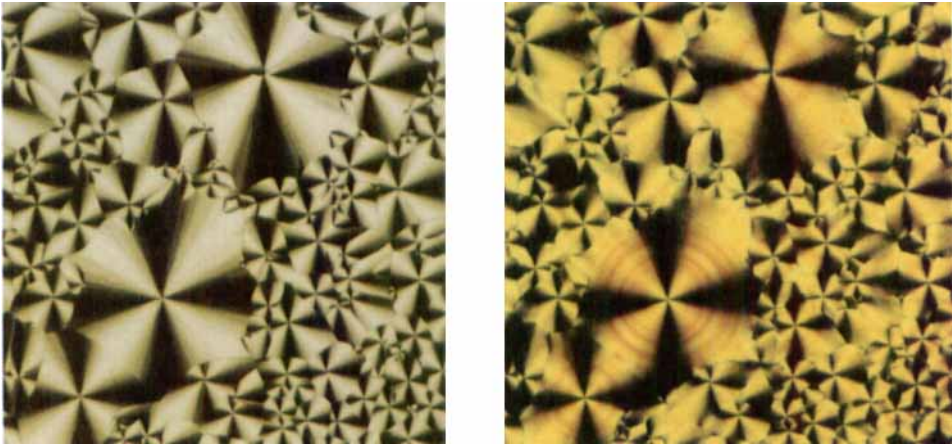
(a) (b)

Figure 2. Optical textures of **7c** between crossed polarizers. (a) At 80°C; (b) at 30°C.
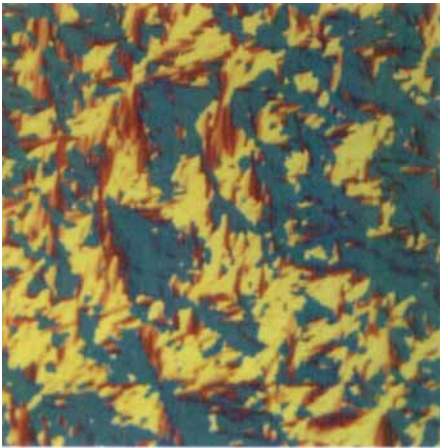
(c) (d)

Figure 4. Optical textures of **10a** between crossed polarizers (λ-plate). (a) At 120°C; (b) at 25°C.

Figure 5. Optical texture (crossed polarizers; λ-plate) of the contact zone between **10a** and **7c** at 100°C.

(a)

(b)

(c)

(d)

Figure 7. Optical textures of **11** between crossed polarizers. (*a*) Cooling, 125°C; (*b*) cooling, 116°C; (*c*) annealing, 116°C; (*d*) heating, 125°C.
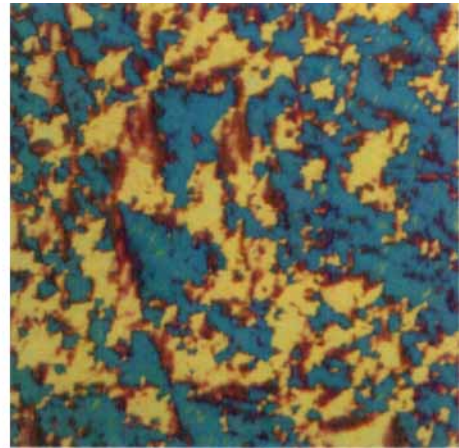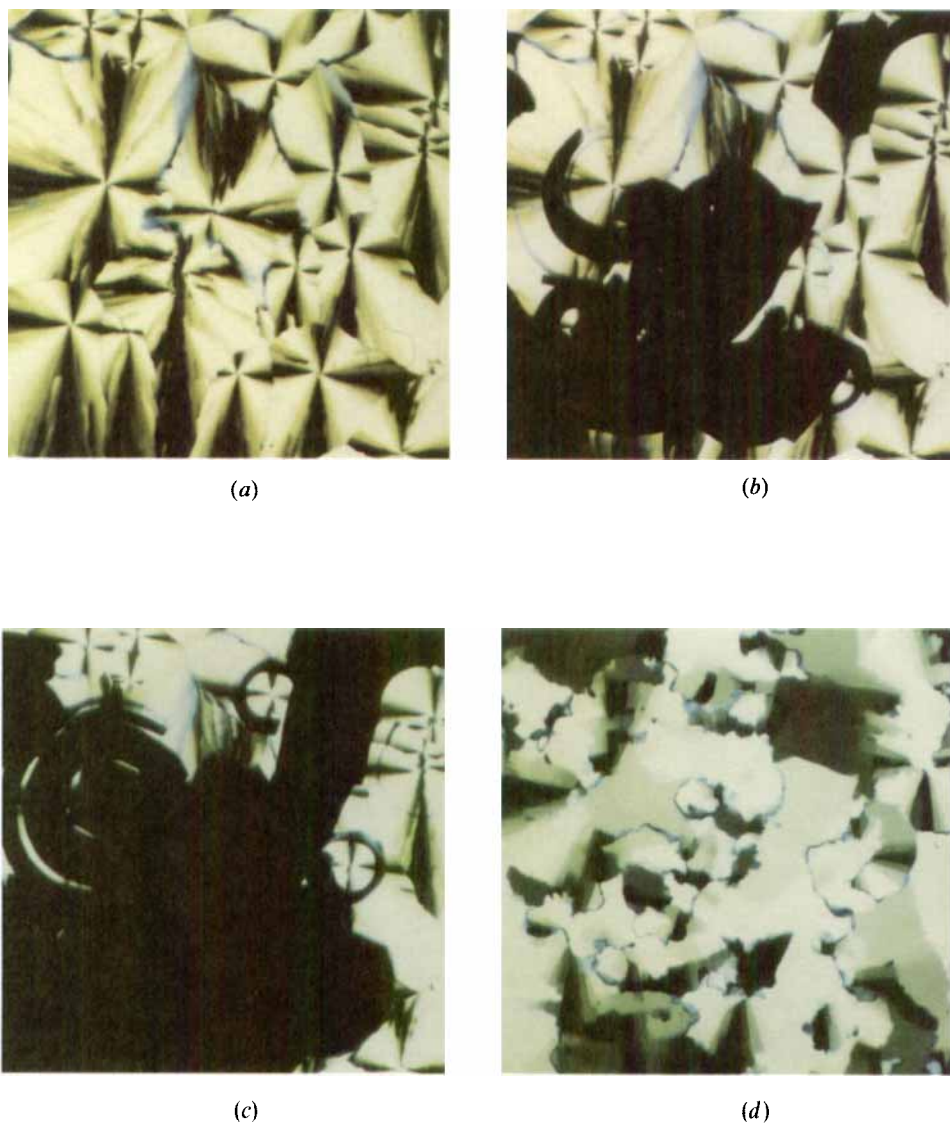
Compared with the monofunctionalized 'two chain' diols **7**, all the siloxane model compounds exhibit higher clearing temperatures (see table 3). This behaviour is typical for liquid crystalline diols and was described earlier by Tschierske for the transformation of a monomeric 1,2-diol to a double headed diol-based mesogen containing four hydroxy groups [14, 15].

As shown representatively for **10a**, a broken focal-conic texture, indicating a columnar mesophase, can be observed by polarizing microscopy for M_3 (see figure 4 (*a*)). Concentric arcs appear in the texture on cooling to M_1 (see figure 4 (*b*)).

As can be seen using X-ray measurements (see table 4), the siloxane twins **10a, b** exhibit only the first order reflection and the corresponding d_{200} second order
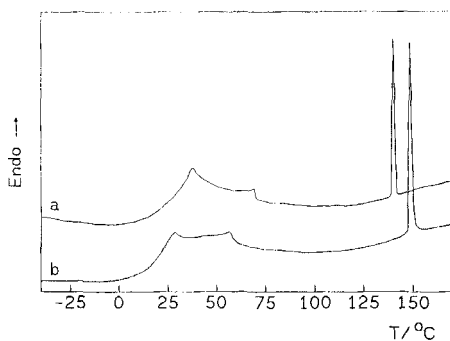
Figure 3. DSC thermogram of the compounds **10** (heating rate 10°C min^{-1}). (*a*) Second heating curve of **10a**; (*b*) second heating curve of **10b**.
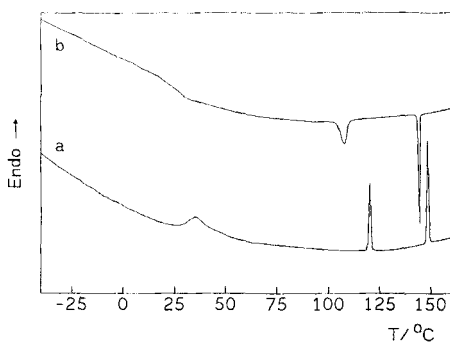

Figure 6. DSC thermogram of compound **11** (heating and cooling rate 10°C min^{-1}). (*a*) Second heating curve; (*b*) cooling curve.

Table 3. Thermal data for compounds **10** and **11** from second heating curves (heating rate 10°C min^{-1}). Transition temperatures (°C) and, in brackets, transition enthalpies (kJ mol^{-1} diol unit). (T_g = glass transition temperature; M_1 = mesophase 1; M_2 = mesophase 2; M_3 = mesophase 3; I = isotropic melt.)

Compound	T_g	M_1		M_2		M_3		I
10a	17	●	69	—		●	140·5 (1·8)	●
10b	18	●	57	—		●	149·0 (1·6)	●
11	28	—		●	120·5 (1·2)	●	148·5 (1·3)	●

Table 4. X-ray data for the hexagonal columnar mesophases of compounds **10a, b**. (T = measuring temperature; d_{hkl} = lattice spacings; a_{hex} = lattice constant calculated from d_{200} value.)

Compound	$T/°C$	$d_{hkl}/Å$		Halo/Å	Halo/Å	$a_{hex}/Å$
		100	200			
10a	107	41·0	21·2	—	4·75	49·0
10b	107	43·3	22·4	7·1	4·75	51·7

reflection. Because there is no d_{110} reflection, no evidence is given for the presumed hexagonal columnar phase. Therefore, additional miscibility experiments, using the contact method, between **10a, b** and **7c** have been performed. Because of the complete miscibility (see figure 5), we can clearly classify the mesophase M_3 of **10a, b** as also being hexagonal columnar. Apparently the linking siloxane units slightly disturb the columnar structure, causing the omission of the d_{110} reflection. Dependent on the number of dimethylsiloxane units, the linking chain leads to a proportional increase in the intercolumnar distance, and also with respect to the diol **7c** (cf. tables 2 and 4).

A second halo at 7·1 Å can be observed for **10b** with six silicon atoms in the linkage group. Normally, this effect is typical for siloxane polymers and is explained there by the scattering behaviour of the polymer main chain [16].

In comparison with the monofunctionalized 'two chain' diols **7** and the siloxane twins **10a, b**, the thermal behaviour of the cyclic model compound **11** differs totally. As shown in figure 6, two weak endothermic peaks, representing two different mesophases, are detectable at 120·5°C ($\Delta H = 1·2$ kJ mol^{-1}) and at 148·5°C ($\Delta H = 1·3$ kJ mol^{-1}) in the heating curve. Furthermore, a glass transition can be observed at 28°C. This phase behaviour can be investigated by polarizing microscopy. First of all, a birefringent pseudo-focal-conic texture (figure 7 (a)), indicating a hexagonal columnar mesophase, appears at 145°C on cooling the sample from 160°C. After cooling to 116°C, a slow formation of an optically isotropic phase can be observed. As shown in figure 7 (b), the geometrically growing domains indicate a cubic structure. The formation of the cubic mesophase is influenced by the previously existing pseudo-focal-conic texture, resulting in curved domains (see figure 7 (c)). A mosaic texture appears on heating the sample from the cubic mesophase into the hexagonal mesophase (see figure 7 (d)).

X-ray measurements confirm both mesophase structures. Detailed spectroscopic data for the cubic and the hexagonal columnar mesophase will be published in the future.

4. Conclusions

By analogy with the liquid crystalline monofunctionalized 'two chain' diols **7**, the siloxane twins **10a, b** form a hexagonal columnar mesophase by aggregation of single molecules via hydrogen bonding. The cyclic siloxane model compound **11** shows an interesting polymorphism. Here, an optically isotropic cubic mesophase is formed below a hexagonal columnar phase. Further investigations will comprise side chain liquid crystalline siloxane polymers with different contents of 'two chain' diol units. Furthermore, the terminal double bond can be used to synthesize diol-containing polymers with other backbones. Thus, the influence of the polymer main chain on mesophase behaviour can be studied.

5. Experimental
5.1. *Instruments*

IR: Bio Rad/Digilab FTS 40. ^{1}H NMR: Bruker AC 250 (250 MHz). ^{13}C NMR: Bruker AC 250 (62·5 MHz). MS: Varian MAT 312. Elemental analysis: Mikroanalytisches Labor Ilse Beetz, Kronach. Polarizing microscopy: Leitz Labolux 12 Pol, Mettler hot stage FP 82, photoautomat Wild MPS 45/51 S. DSC: Perkin–Elmer DSC 7 (temperatures were taken from peak maxima). X-ray: Simens Θ-Θ goniometer, X-ray tube FK 60-20, scintillation counter NIM, temperature controller TTK-HC.

5.2. *Materials*

Vanillic acid nitrile (Janssen), 1-bromodecane (Fluka), 1-bromoundecane (Fluka), powdered potassium carbonate (Riedel de Häen), sodium cyanide (Fluka), phenylboric acid (Fluka), 1,1,3,3-tetramethyldisiloxane **8a** (ABCR), 1,3,5,7-tetramethylcyclotetrasiloxane **9** (Alfa) were purchased commercially. 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethylhexasiloxane **8b** ($n \approx 5$ means a mixture of oligomers with 86 per cent $n = 5$) and the dichloro(endo-dicyclopentadiene)-platinum(II) catalyst were kindly supplied by Wacker Chemie. Silica gel 60 (E. Merck) was used to purify compounds by column chromatography. 3-Phenyl-2,4-dioxa-3-bora-bicyclo[3.3.1]-nonan-7-ol and 11-bromoundec-1-ene were synthesized according to the literature [17, 18].

5.3. *Synthesis and characterization*

1: The etherification reaction of vanillic acid nitrile was carried out as described earlier [10].

1a: Yield: 88 per cent, white crystals. Melting point: 62–65°C. ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·87 (t; 3 H, –CH$_3$), 1·1–1·5 (br; 14 H, CH$_2$–), 1·83 (quint.; 2 H, OCH$_2$CH$_2$–), 3·85 (s; 3 H, –OCH$_3$), 4·03 (t; 2 H, OCH$_2$–), 6·87 (d; 1 H, aromatic, 5-position; $J = 8$ Hz), 7·06 (d; 1 H, aromatic, 2-position; $J = 2$ Hz), 7·13 (dd; 1 H, aromatic, 6-position; $J = 8$ Hz $+ 2$ Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) = 14·0, 22·5, 25·8, 28·8, 29·2, 29·4, 31·8, 56·1, 69·1, 103·5, 112·2, 114·2, 119·3, 126·3, 149·4, 152·5. IR (KBr, cm^{-1}): 2961, 2949, 2941, 2916, 2864, 2847, 2224, 1597, 1582, 1516, 1466, 1275, 1244, 1167, 1140, 1030, 1022, 876, 810, 617. MS (m/e): 289 (12 per cent), 149 (100 per cent). C$_{18}$H$_{27}$NO$_2$ (289·42) Calculated (per cent): C 74·70, H 9·40, N 4·84, O 11·06; Found (per cent): C 74·73, H 9·38, N 4·85.

1b: Yield: 95 per cent, white crystals. Melting point: 59–61°C. ^{1}H NMR (CDCl$_3$): δ (ppm) = 1·15–1·55 (br; 12 H, CH$_2$–), 1·83 (quint.; 2 H, OCH$_2$CH$_2$–), 2·03 (q; 2 H, =CH–CH$_2$–), 3·87 (s; 3 H, –OCH$_3$), 4·03 (t; 2 H, OCH$_2$–), 4·95 (m; 2 H, –CH=CH$_2$), 5·80 (m; 1 H, –CH=CH$_2$), 6·87 (d; 1 H, aromatic, 5-position; $J = 8$ Hz), 7·05 (d; 1 H, aromatic, 2-position, $J = 2$ Hz), 7·23 (dd, 1 H, aromatic, 6-position, $J = 8$ Hz $+ 2$ Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) = 25·7, 28·7, 28·9, 29·1, 29·2, 29·3, 33·6, 56·0, 69·0, 103·4, 112·1, 114·0, 114·1, 119·2, 126·2, 139·0, 149·3, 152·4. IR (KBr, cm^{-1}): 2920, 2851, 2224, 1641, 1597, 1580, 1518, 1468, 1412, 1335, 1279, 1242, 1140, 1026, 926, 864, 812, 619. MS (m/e): 301 (18 per cent), 149 (100 per cent). C$_{19}$H$_{27}$NO$_2$ (301·43) Calculated (per cent): C 75·71, H 9·03, N 4·65, O 10·62; Found (per cent): C 75·98, H 8·90, N 4·53.

2: According to the literature [11], 10 ml of **1** were dissolved in 20 ml of dry DMSO in a 50 ml Schlenk tube with a nitrogen inlet. Then, 50 mmol of sodium cyanide were added and the solution was stirred at 150°C for 10 h. The hot reaction solution was poured into 50 ml of ice water. With vigorous stirring, 10 ml of concentrated HCl were added (caution HCN evolution is possible). The resulting precipitate was filtered off and washed with 300 ml of water. After drying *in vacuo* at 40°C, the crude product was purified by column chromatography (eluent: hexane/ethyl acetate; volume ratio 4 : 1) followed by recrystallization from hexane.

2a: Yield: 67 per cent, colourless crystals. Melting point: 63–66°C. ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·87 (t; 3 H, –CH$_3$), 1·15–1·55 (br; 14 H, CH$_2$–), 1·83 (quint; 2 H, OCH$_2$CH$_2$–), 4·08 (t; 2 H, OCH$_2$–), 5·75 (s; 1 H, –OH), 6·83 (d; 1 H, aromatic, 5-position; $J = 8$ Hz), 7·15 (m; 2 H, aromatic, 2 + 6-position). ^{13}C NMR (CDCl$_3$): δ (ppm) = 14·0, 22·5, 25·8, 28·8, 29·2, 29·4, 31·8, 69·2, 104·0, 111·4, 117·4, 119·0, 125·4, 146·0, 149·8. IR (KBr, cm^{-1}): 3375, 2947, 2924, 2851, 2230, 1614, 1512, 1476, 1279, 1242, 1196, 1125, 1013, 890, 796, 607. MS (m/e): 275 (50 per cent), 135 (100 per cent). C$_{17}$H$_{25}$NO$_2$ (275·39)

Calculated (per cent): C 74·14, H 9·15, N 5·09. O 11·62; Found (per cent): C 74·09, H 9·05, N 5·12.

2b: Yield: 69 per cent, colourless crystals. Melting point: 52–55°C. ^{1}H NMR (CDCl$_3$): δ (ppm) = 1·15–1·55 (m; 12 H, CH$_2$–), 1·83 (quint; 2 H, OCH$_2$CH$_2$–), 2·03 (q; 2 H, =CH–CH$_2$–), 4·08 (t; 2 H, OCH$_2$–), 4·95 (m; 2 H, –CH=CH$_2$), 5·80 (m; 2 H, –CH= CH$_2$ + –OH), 6·83 (d; 1 H, aromatic, 5-position; $J = 8$ Hz), 7·15 (m; 2 H, aromatic, 2 + 6-position). ^{13}C NMR (CDCl$_3$): δ (ppm) = 25·8, 28·8, 29·0, 29·2, 29·3, 29·4, 33·7, 69·2, 104·1, 111·5, 114·1, 117·5, 119·0, 125·5, 139·1, 145·9, 149·7. IR (KBr, cm^{-1}): 3370, 2947, 2926, 2853, 2226, 1644, 1604, 1582, 1506, 1476, 1281, 1246, 1200, 1126, 1009, 951, 907, 891, 804, 793. MS (*m/e*): 287 (46 per cent), 135 (100 per cent). C$_{18}$H$_{25}$NO$_2$ (287·40) Calculated (per cent): C 75·23, H 8·77, N 4·87, O 11·13; Found (per cent): C 75·31, H 8·69, N 4·83.

3: The etherification of **2** was carried out as described earlier [10].

3a: Yield: 87 per cent, white crystals. Melting point: 69–70°C. ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·88 (t; 3 H, –CH$_3$), 1·10–1·55 (br; 26 H, CH$_2$–), 1·80 (br; 4 H, OCH$_2$CH$_2$–), 2·03 (q; 2 H, =CH–CH$_2$–), 3·97 (2 × t; 4 H, OCH$_2$–), 4·95 (m; 2 H, –CH=CH$_2$), 5·80 (m; 1 H, –CH=CH$_2$), 6·83 (d; 1 H, aromatic, 5-position; $J = 8$ Hz), 7·04 (d; 1 H, aromatic, 2-position; $J = 2$ Hz), 7·22 (dd; 1 H, aromatic, 6-position; $J = 8$ Hz + 2 Hz). ^{13}C NMR CDCl$_3$): δ (ppm) = 14·0, 22·6, 25·9, 28·9, 29·0, 29·1, 29·3, 29·4, 29·5, 31·8, 33·7, 69·0, 69·4, 103·5, 112·7, 114·1, 116·0, 119·4, 126·2, 139·1, 149·0, 153·0. IR (KBr, cm^{-1}): 2957, 2918, 2872, 2849, 2220, 1597, 1516, 1468, 1279, 1244, 1138. MS (*m/e*): 427 (100 per cent). C$_{28}$H$_{45}$NO$_2$ (427·67) Calculated (per cent): C 78·64; H 10·61, N 3·28, O 7·48; Found (per cent): C 78·63, H 10·64, N 3·40.

3b: Yield: 89 per cent, white crystals. Melting point: 70–71°C. ^{1}H NMR (CDCl$_3$), ^{13}C NMR (CDCl$_3$) and IR (KBr) correspond to **3a**. MS (*m/e*): 427 (100 per cent). C$_{28}$H$_{45}$NO$_2$ (427·67) Calculated (per cent): C 78·64, H 10·61, N 3·28, O 7·48; Found (per cent): C 78·77, H 10·58, N 3·17.

3c: Yield: 95 per cent, white crystals. Melting point: 70–72°C. ^{1}H NMR (CDCl$_3$) (except δ (ppm) = 1·10–1·55 (br; 28 H, CH$_2$–)), ^{13}C NMR (CDCl$_3$) and IR (KBr) correspond to **3a**. MS (*m/e*): 441 (100 per cent). C$_{29}$H$_{47}$NO$_2$ (441·70) Calculated (per cent): C 78·86, H 10·72, N 3·17, O 7·24; Found (per cent): C 78·75, H 10·67, N 3·12.

4: The saponification of the nitriles **3** was carried out as described in the literature [19]. 10 mmol of nitrile, 200 mmol of KOH and 50 ml of triethylene glycol were placed in a Schlenk tube with a nitrogen inlet and heated under vigorous stirring for 15 h to 150°C. When the evolution of ammonia, indicating the progress of the saponification, had finished, the solution was poured into 300 ml of water. The solution was acidified by adding 20 ml of concentrated HCl. The coloured precipitate was filtered off and washed with 1000 ml of water to remove all triethylene glycol. The residue was dried overnight at 60°C *in vacuo*. Purification was carried out by recrystallization twice from 150 ml of ethanol at room temperature.

4a: Yield: 79 per cent, white crystals. Melting point: 112–114°C. ^{1}H NMR(CDCl$_3$): δ (ppm) = 0·88 (t; 3 H, –CH$_3$), 1·10–1·55 (br; 26 H, CH$_2$–), 1·82 (br; 4 H, OCH$_2$CH$_2$–), 2·03 (q; 2 H, =CH–CH$_2$–), 4·02 (2 × t; 4 H, OCH$_2$–), 4·93 (m; 2 H, –CH=CH$_2$), 5·80 (m; 1 H, –CH=CH$_2$), 6·88 (d; 1 H, aromatic, 5-position; $J = 8$ Hz), 7·58 (d; 1 H, aromatic, 2-position; $J = 2$ Hz), 7·72 (dd; 1 H, aromatic, 6-position; $J = 8$ Hz + 2 Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) = 14·0, 22·6, 26·0, 28·9, 29·1, 29·3, 29·5, 31·9, 33·8, 69·1, 69·3, 112·0, 114·1, 114·8, 121·5, 124·5, 139·1, 148·6, 154·1, 172·1. IR (KBr, cm^{-1}): 2926, 2849, 1678, 1670, 1595, 1586, 1443, 1306, 1277, 1227, 1140, 770. MS (*m/e*): 446 (20 per cent), 154 (100 per cent). C$_{28}$H$_{46}$O$_4$ (446·67) Calculated (per cent): C 75·29, H 10·38, O 14·33; Found (per cent): C 75·27, H 10·38.

4b: Yield: 77 per cent, white crystals. Melting point: 111–113°C. ^{1}H NMR (CDCl$_3$), ^{13}C NMR (CDCl$_3$) and IR (KBr) correspond to **4a**. MS (m/e): 446 (80 per cent), 154 (100 per cent). C$_{28}$H$_{46}$O$_4$ (446·67) Calculated (per cent): C 75·29, H 10·38, O 14·33; Found (per cent): C 75·37, H 10·16, O 14·30.

4c: Yield: 87 per cent, white crystals. Melting point: 113–115°C. ^{1}H NMR (CDCl$_3$) except (δ (ppm) = 1·10–1·55 (br; 28 H, CH$_2$–)), ^{13}C NMR (CDCl$_3$) and IR (KBr) correspond to **4a**. MS (m/e): 460 (80 per cent), 154 (100 per cent). C$_{29}$H$_{48}$O$_4$ (460·69) Calculated (per cent): C 75·61, H 10·50, O 13·89; Found (per cent): C 75·77, H 10·30, O 14·05.

5: The acid chlorides **5** were synthesized according to the literature and used without further purification [19].

6: The phenylboric acid derivatives were synthesized as described earlier [6] and deprotected without preceding purification.

6c: The monomer unit was reprotected by dissolving 10 mmol of compound **7c** and 11 mmol of phenylboric acid in 500 ml of dry dioxan. The dioxan solvent was distilled off under normal pressure until a small residue of 50 ml remained, to remove the water, which was formed during the reaction. The residual dioxan was removed under high vacuum. The resulting slightly yellow oil was dissolved in 30 ml of hexane and put into a freezer overnight. The small amount of colourless crystals so obtained was filtered off and washed with 5 ml of cold hexane. The hexane was removed from the filtrate and washings under reduced pressure and the oily product was dried overnight under high vacuum.

Yield: 95 per cent, slightly yellow oil, slowly crystallizing. Melting point: 37–42°C. ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·88 (t; 3 H, –CH$_3$), 1·10–1·50 (br; 28 H, CH$_2$–), 1·82 (m; 4 H, OCH$_2$CH$_2$–), 1·80–2·12 (m, 5 H, HCH$_{ax}$. + =CH–CH$_2$–), 2·26 (m; 1 H, HCH$_{eq}$.–), 2·57 (m; 2 H, HCH$_{eq}$.–), 3·72 (t; 2 H, OCH$_2$–), 3·83 (t; 2 H, OCH$_2$–), 4·57 (br; 2 H, –CH–OB), 4·95 (m; 2 H, –CH=CH$_2$), 5·46 (m; 1 H, –CH–OOC), 5·80 (m; 1 H, –CH=CH$_2$), 6·01 (d; 1 H, aromatic, 5-position, $J = 8$ Hz), 6·94 (dd; 1 H, aromatic, 6-position, $J = 8$ Hz + 2 Hz), 7·15–7·50 (m; 4 H, aromatic, 2-position + phenylboric 3 + 4-position), 7·74 (m; 2 H, phenylboric 2-position). ^{13}C NMR (CDCl$_3$): δ (ppm) = 14·1, 22·6, 25·9, 28·9, 29·1, 29·3, 29·4, 29·5, 29·6, 31·9, 33·2, 33·7, 35·8, 64·8, 67·3, 68·6, 68·8, 111·1, 113·8, 114·1, 121·6, 124·0, 127·4, 130·1, 133·8, 139·1, 148·1, 152·6, 166·0. IR (film, cm^{-1}): 2926, 2855, 1707, 1601, 1508, 1456, 1442, 1429, 1415, 1342, 1306, 1287, 1269, 1244, 1211, 1155, 1074, 764, 700, 642. MS (m/e): 660 (100 per cent). C$_{41}$H$_{61}$BO$_6$ (660·74) Calculated (per cent): C 74·53, H 9·31, B 1·64, O 14·53; Found (per cent): C 74·15, H 9·15, O 15·00.

7: The hydrolysis was carried out according to the literature [6]. All diol compounds were purified by column chromatography with ethyl acetate as eluent and freeze dried once from benzene solution. Directly after this procedure, the diols **7a–c** were obtained as waxy products at room temperature. Melting points (cf. table 1) have been obtained by DSC measurements after cooling to −50°C.

7a: Yield: 65 per cent. ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·87 (t; 3 H, –CH$_3$), 1·10–2·15 (br; 37 H, CH$_2$– + OCH$_2$CH$_2$– + HCH$_{ax}$. + OH + =CH–CH$_2$–), 2·30 (m; 3 H, HCH$_{eq}$.–), 3·83 (m; 2 H, –CH–OH), 4·02 (2 × t; 4 H, OCH$_2$–), 4·95 (m; 3 H, –CH=CH$_2$ + –CH–OOC), 5·80 (m; 1 H, –CH=CH$_2$), 6·83 (d; 1 H, aromatic, 5-position, $J = 8$ Hz), 7·50 (d; 1 H, aromatic, 2-position, $J = 2$ Hz), 7·62 (dd; 1 H, aromatic, 6-position, $J = 8$ Hz + 2 Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) = 14·0, 22·6, 25·9, 26·0, 28·9, 29·0, 29·1, 29·2, 29·3, 29·4, 29·5, 31·8, 33·7, 39·8, 43·3, 65·3, 68·3, 68·9, 69·3, 111·8, 114·0, 114·3, 122·1, 123·6, 139·1, 148·4, 153·4, 166·0. IR (KBr, cm^{-1}): 3478, 2922, 2851, 1705, 1601, 1516, 1468, 1431, 1294, 1273, 1225, 1140, 1111, 1031, 990, 760. MS (m/e): 560 (100 per cent).

$C_{34}H_{56}O_6$ (560·81) Calculated (per cent): C 72·82, H 10·06, O 17·12; Found (per cent): C 72·69, H 10·04, O 17·07.

7b: Yield: 85 per cent. ^{1}H NMR (CDCl$_3$), ^{13}C NMR (CDCl$_3$) and IR (KBr) correspond to **7a**. MS (m/e): 560 (100 per cent). $C_{34}H_{56}O_6$ (560·81) Calculated (per cent): C 72·82, H 10·06, O 17·12; Found (per cent): C 72·90, H 9·94, O 17·04.

7c: Yield: 80 per cent. ^{1}H NMR (CDCl$_3$) (except δ (ppm) = 1·10–1·93 (br; 37 H, CH$_2$– + OCH$_2$CH$_2$– + HCH$_{ax.}$ + OH), 2·02 (q.; 2 H, =CH–CH$_2$–)), ^{13}C NMR (CDCl$_3$) and IR (KBr) correspond to **7a**. MS (m/e): 574 (100 per cent). $C_{35}H_{58}O_6$ (574·84) Calculated (per cent): C 73·13, H 10·17, O 16·70; Found (per cent): C 73·07, H 10·36, O 16·90.

10: The hydrosilylation reaction and deprotection were carried out as described earlier [10]. All model compounds were purified as described below and were dried in a vacuum shelf drier at 95°C over phosphorus pentaoxide.

10a: Yield: 57 per cent, slightly brownish solid. Purification: Column chromatography with ethyl acetate followed by recrystallization from ethyl acetate with refrigeration. ^{1}H NMR (CDCl$_3$): δ(ppm) = 0·00 (s; 12 H, –SiCH$_3$), 0·48 (br; 4 H, –SiCH$_2$–), 0·88 (t; 6 H, –CH$_3$), 1·00–2·12 (br; 82 H, CH$_2$– + HCH$_{ax.}$ + OH), 2·28 (m; 6 H, HCH$_{eq.}$–), 3·83 (m; 4 H, –CH–OH), 4·00 (2 × t; 8 H, OCH$_2$–), 4·98 (m; 2 H, –CH–OOC), 6·83 (d; 2 H, aromatic, 5-position, J = 8 Hz), 7·50 (d; 2 H, aromatic, 2-position, J = 2 Hz), 7·60 (dd; 2 H, aromatic, 6-position, J = 8 Hz + 2Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) = 0·4, 14·1, 18·4, 22·6, 23·3, 26·0, 29·1, 29·2, 29·3, 29·4, 29·6, 31·9, 33·4, 39·8, 43·1, 65·6, 68·2, 69·0, 69·3, 111·9, 114·3, 122·3, 123·6, 148·5, 153·4, 165·9. IR (KBr, cm^{-1}): 3480, 2922, 2851, 1703, 1601, 1518, 1468, 1431, 1314, 1292, 1275, 1254, 1225, 1142, 1111, 1066, 1032, 999, 760. MS (m/e): 1282 (0·5 per cent), 73 (100 per cent). $C_{74}H_{130}O_{13}Si_2$(1284·00) Calculated (per cent): C 69·22, H 10·20, O 16·20, Si 4·37; Found (per cent): C 69·28, H 10·21, Si 4·67.

10b: Yield: 54 per cent, slightly brownish solid. Purification: Column chromatography with ethyl acetate/acetone (volume ratio 2/1). ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·03 (3 × s; 36 H, –SiCH$_3$), 0·52 (br; 4 H, –SiCH$_2$–), 0·87 (t; 6 H, –CH$_3$), 1·00–2·00 (br; 82 H, CH$_2$– + HCH$_{ax.}$ + OH), 2·28 (m; 6 H, HCH$_{eq.}$–), 3·84 (m; 4 H, –CH–OH), 4·01 (2 × t; 8 H, OCH$_2$–), 4·98 (m; 2 H, –CH–OOC), 6·83 (d; 2 H, aromatic, 5-position, J = 8 Hz), 7·50 (d; 2 H, aromatic, 2-position, J = 2 Hz), 7·62 (dd; 2 H, aromatic, 6-position, J = 8 Hz + 2 Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) = 0·1, 1·0, 1·1, 14·1, 18·2, 22·6, 23·2, 26·0, 29·1, 29·2, 29·3, 29·4, 29·6, 31·9, 33·4, 39·8, 43·2, 65·5, 68·2, 69·0, 69·3, 111·9, 114·4, 122·3, 123·6, 148·5, 153·4, 165·9. IR (KBr, cm^{-1}): 3354, 2922, 2853, 1709, 1599, 1514, 1468, 1431, 1292, 1271, 1260, 1217, 1136, 1090, 1028, 839, 800, 764. MS (m/e): 1579 (1 per cent), 73 (100 per cent). For the monodisperse product **10b** with $n = 5$: $C_{82}H_{154}O_{17}Si_6$ (1580·62) Calculated (per cent): C 62·31, H 9·82, O 17·21, Si 10·66; Found for $n \approx 5$ (per cent): C 61·94, H 9·46, Si 10·51.

11: Yield: 66 per cent, slightly brownish solid. Purification: Column chromatography with ethyl acetate to extract all impurities, followed by THF, to wash out the product. ^{1}H NMR (CDCl$_3$): δ (ppm) = 0·04 (s; 12 H, –SiCH$_3$), 0·50 (br; 8 H, –SiCH$_2$–), 0·87 (t; 12 H, –CH$_3$), 1·00–2·00 (br; 164 H, CH$_2$– + HCH$_{ax.}$ + OH), 2·28 (br; 12 H, HCH$_{eq.}$–), 3·65–4·05 (br; 24 H, OCH$_2$– + –CH–OH), 4·98 (br; 4 H, –CH–OOC), 6·83 (br; 4 H, aromatic, 5-position), 7·50 (br; 4 H, aromatic, 2-position), 7·62 (br; 4 H, aromatic, 6-position). ^{13}C NMR (CDCl$_3$): δ (ppm) = – 0·6, 14·1, 17·2, 22·7, 23·0, 26·0, 29·1, 29·2, 29·4, 29·6, 30·3, 31·9, 33·2, 39·7, 43·0, 65·7, 68·1, 69·0, 69·3, 111·9, 114·4, 122·4, 123·6, 148·5, 153·4, 165·8. IR (KBr, cm^{-1}): 3647, 3374, 2920, 2853, 1707, 1599, 1516, 1468, 1431, 1294, 1273, 1215, 1144, 1078, 1026, 1001, 766. $C_{144}H_{248}O_{28}Si_4$ (2539·86) Calculated (per cent): C 68·10, H 9·84, O 17·64, Si 4·42; Found (per cent): C 68·15, H 9·70, Si 4·46.

References

[1] DESTRADE, C., TINH, N. H., ROUBINEAU, A., and LEVELUT, A. M., 1988, *Molec. Crystals liq. Crystals*, **159**, 163.

[2] LATTERMANN, G., 1989, *Liq. Crystals*, **6**, 619.

[3] LATTERMANN, G., 1990, *Molec. Crystals liq. Crystals*, **182B**, 299.

[4] LATTERMANN, G., and STAUFER, G., 1990, *Molec. Crystals liq. Crystals*, **191**, 199.

[5] STAUFER, G., 1990, Ph.D. thesis, Bayreuth.

[6] LATTERMANN, G., and STAUFER, G., 1989, *Liq. Crystals*, **4**, 347.

[7] EBERT, M., KLEPPINGER, R., SOLIMAN, M., WOLF, M., WENDORFF, J. H., LATTERMANN, G., and STAUFER, G., 1990, *Liq. Crystals*, **7**, 553.

[8] LATTERMANN, G., STAUFER, G., and BREZESINSKI, G., 1991, *Liq. Crystals*, **10**, 169.

[9] FESTAG, R., KLEPPINGER, R., SOLIMAN, M., WENDORFF, J. H., LATTERMANN, G., and STAUFER, G., 1992, *Liq. Crystals*, **11**, 699.

[10] STAUFER, G., and LATTERMANN, G., 1991, *Makromolek. Chem.*, **192**, 2421.

[11] MCCARTHY, J. R., MOORE, J. L., and CREGGE, R. J., 1978, *Tetrahedron Lett.*, **52**, 5183.

[12] BHATT, M. V., and KULKARNI, S. U., 1983, *Synthesis*, 249.

[13] BEGINN, U., and LATTERMANN, G., 1994, *Molec. Crystals liq. Crystals* (in the press).

[14] TSCHIERSKE, C., and ZASCHKE, H., 1990, *J. chem. Soc. chem. Commun.*, p. 1013.

[15] HENTRICH, F., TSCHIERSKE, C., and ZASCHKE, H., 1991, *Angew. Chem. Int. Ed.*, **30**, 440.

[16] DIELE, S., OELSNER, S., KUSCHEL, F., HISGEN, B., and RINGSDORF, H., 1988, *Molec. Crystals liq. Crystals*, **155**, 399.

[17] STRONG, P. N., and KEANA, J. F. W., 1975, *J. org. Chem.*, **40**, 956.

[18] MARVEL, C. S., and GARRISON, W. E., JR., 1959, *J. Am. chem. Soc.*, **81**, 4737.

[19] SCHWETLICK, K. (editor), 1986, *Organikum* (VEB Deutscher Verlag der Wissenschaften), p. 423.