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Dimesogenic liquid crystalline oligosiloxanes

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In this paper, the syntheses, phase properties and ferroelectric properties of new liquid crystalline oligosiloxane dimesogens are described. Smectic phases are dominant in this class of materials. Spontaneous polarizations are in the range of 10 to approximately 100 nC cm^{-2}. The materials show interesting properties for display applications. Although offering higher mechanical stability than low molar mass materials, their switching is significantly faster (switching times in the range of some 10^{-5} s) than is the case for similar side group polymers (typically some 10^{-3} s). Therefore these new oligosiloxane derivatives may be ideal for building flexible displays. In addition, mixtures of oligosiloxane dimesogens were compared with copolymers and with siloxane-free low molar mass materials bearing the same mesogenic groups. The results support the idea of a 'virtual polymer backbone', which is formed by a microphase separation phenomenon. Dimesogenic siloxane mixtures and copolymers behave quite similarly, while the siloxane-free mixtures show a different phase behaviour.

1. Introduction

In a few recent publications, the fixation of mesogenic groups to oligomeric siloxanes is described [1, 2]. Due to microphase phenomena in siloxanes [3, 4], the structures of oligomeric and polymeric materials are very similar. Therefore a 'virtual polymer backbone' is postulated to appear in the oligomeric siloxanes [2]. This idea is illustrated in figure 1. Here we want to describe the synthesis of new oligomeric siloxanes and the investigation of their properties. In contrast to systems previously described [2], their siloxane backbone shows a broad polydispersity (3 to 18 repeat units), which helps them to be more polymer-like, for example, by favouring the glassy state instead of crystallization. Siloxane copolymers and mixtures of oligomeric siloxanes are compared to verify the hypothesis of the virtual polymer backbone. If the assumption is correct, mixtures of oligomeric siloxanes bearing different mesogenic groups should behave like 'virtual copolymers', i.e. show similar phase properties to the copolymers. In display applications, such materials could offer advantages compared to low molar mass mixtures: Complete miscibility is probable even if mesogenic groups with very different structures are used. On the other hand, the oligomeric siloxanes may open a way to more mechanically stable displays than low molar mass materials. Thus they may be ideal materials for flexible displays [5]. In addition, the long switching times of polymers can be avoided.

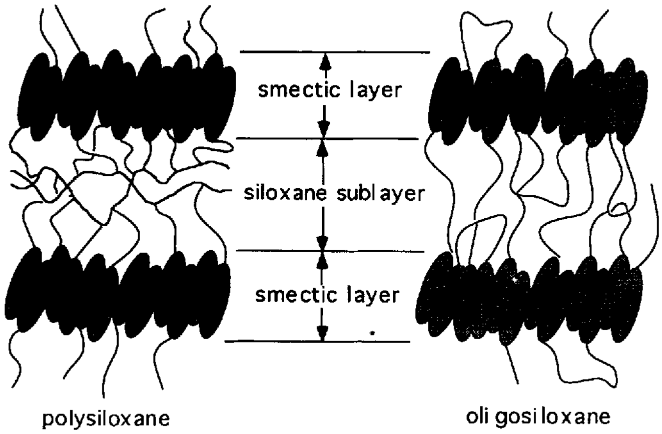

Figure 1. Formation of analogous structures in liquid crystalline oligosiloxanes and polysiloxanes.

In this article, the syntheses and the phase properties of liquid crystalline oligosiloxane derivatives, as well as copolymers and mixtures of oligomeric compounds bearing the same mesogenic groups, are described. The phase behaviour of the two groups of materials is compared and in addition, a comparison with non-siloxane low molar mass mixtures is made.

2. Synthesis

The materials are synthesized according to well-known procedures. Synthetic routes to the alkene precursors **1** and **2** and relevant physical data are described in [6]; the

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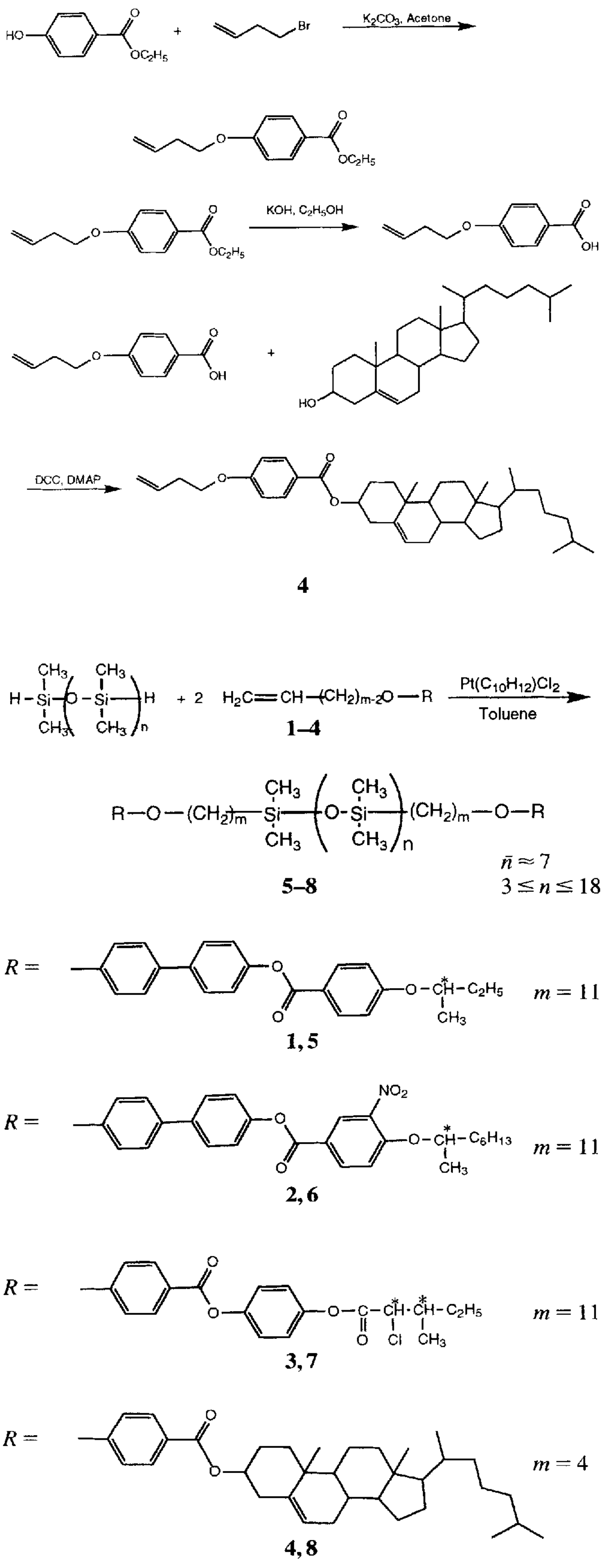


synthetic route and the physical data for alkene precursor **3** can be found in [7]. The syntheses of cholesteryl 4-(but-3-enyloxy)benzoate **4** and the siloxane materials are shown in the reaction scheme.

3. Phase properties

The mesophase sequences of the materials were investigated by polarization microscopy and differential scanning calorimetry (Perkin–Elmer DSC 7, heating and cooling rate 20°C min^{-1}).

The mesophase properties of the four dimesogenic siloxanes are discussed first. The phase sequences are shown in table 1. Three materials show the chiral smectic C* phase. In the case of **5**, no other mesophase is present. The materials **6** and **7** additionally exhibit smectic A phases. Only the cholesterol derivative **8** does not show a chiral smectic C*; the phase is exclusively a S_A phase.

In table 2, the phase sequences of analogous side group polymers incorporating the alkene precursors **1** to **3** are listed. The similarity of the phase properties of the analogous system is evident. However, there are also differences. The transition temperatures of the dimesogenic siloxanes are generally lower and usually they do not form higher ordered smectic phases, which are found in case of the polymers. It is thus possible to obtain materials with a mobile chiral smectic C* phase or a glassy frozen S_C^* phase at room temperature. In a following step, mixtures of the dimesogenic siloxanes **6** and **8** (see table 1) and analogous copolymers (for structures see tables 2 and 3) have been prepared. Again, a comparison of the phase properties of these systems supports the idea of a 'virtual polymer backbone'. Significant similarities are revealed here as illustrated by the phase diagrams for both systems as a function of composition as shown in figure 2. In both cases, materials with a low amount of cholesteryl derivative exhibit a smectic C* phase and a smectic A phase. When the content of cholesteryl derivative is raised, the copolymers and the mixtures show only S_A phases.

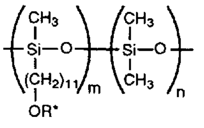
Although the phase behaviour of the two systems is very similar, there are some differences: The glass transition temperatures of the mixtures are generally lower (approximately −20°C compared to 0°C).

Table 1. Phase sequences of the dimesogenic oligosiloxanes.

Siloxane	Phase sequence
5	g 79 S_C^* 128 I
6	g −22 S_C^* 80 S_A 114 I
7	S_x 18 S_C^* 38 S_A 62 I
8	g −15 S_A 133 I

Temperatures are given in °C. g: glassy state. S_x: higher ordered smectic phase, not further identified. S_C^*: chiral smectic C phase. S_A: smectic A phase. I: isotropic.

Table 2. General structure and phases sequences of the analogous side group polymers.



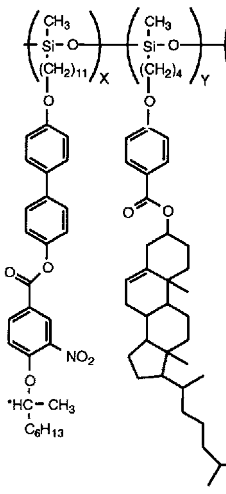
$m{:}n = 1{:}2{\cdot}7$

$m + n \approx 90$

All polymers are statistical copolymers.

Polymer	Mesogen	Phase sequence
P1	1	g 34 S_X 74 S_C^* 115 S_A 131 I
P2	2	g 0 S_X 46 S_C^* 98 S_A 144 I [4]
P3	3	g −26 C 18 S_C^* 85 I [7]

Table 3. General structure and phase sequences of the copolymers with two different mesogenic side groups.

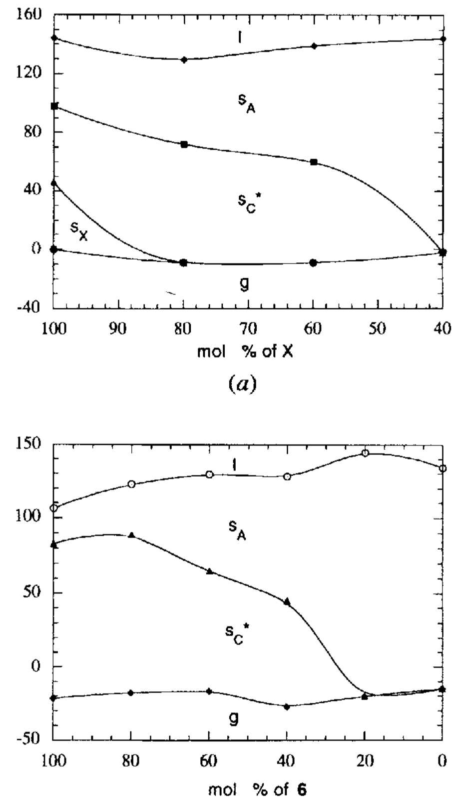


$(X+Y){:}Z = 1{:}2{\cdot}7$
$X+Y+Z \approx 90$

All polymers are statistical copolymers.

Polymer	$X{:}Y$	Phase sequence
P4	80:20	g −9 S_C^* 80 S_A 129·5 I
P5	60:40	g −9 S_C^* 60 S_A139 I
P6	40:60	g −2 S_A 144 I

In the case of the mixtures, the S_C^* phase is observed for up to 60 mol % of the cholesteryl derivative, while in the copolymer systems it was only observed for up to 40 mol % of cholesteryl derivative, maximum. This effect is not caused by phase separation phenomena in the case of the mixtures. No phase separation can be detected by polarization microscopy and the DSC data do not show the transitions of the two compounds separately, but reveal new transitions at different temperatures.



(*a*)

(*b*)

Figure 2. Phase diagram of (*a*) the copolymers **P2**, **P4**, **P5**, and **P6** and (*b*) mixtures of the dimesogenic siloxanes **6** and **8**.

The comparison of mixtures of the dimesogenic siloxanes with mixtures of their low molar mass precursors is also very instructive. The phase diagram of these low molar mass mixtures, which are devoid of the compatibilizing siloxane unit, is shown in figure 3. Here, significant differences from the other systems investigated are obvious. Below their LC phases, the materials crystallize instead of forming a glassy state. The S_C^* phase occurs, but the temperature range and the composition range of its existence are rather small. Going to higher amounts of chloresteryl derivative, cholesteric (N*) and blue phases appear which are found neither in the copolymers nor in the dimesogenic siloxane mixtures.

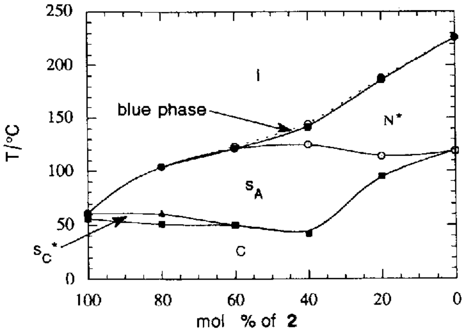


Figure 3. Phase diagram of mixtures of the low molar mass precursors **2** and **4**.

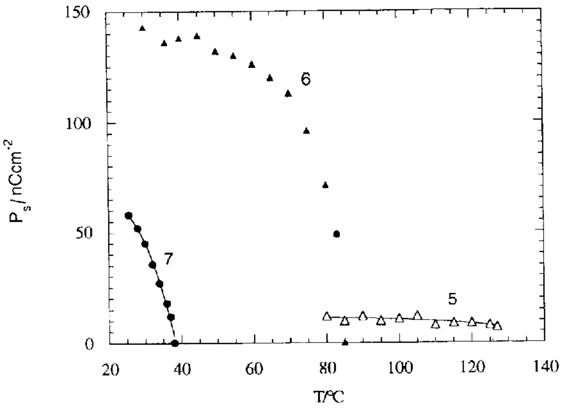


Figure 4. Spontaneous polarizations of the dimesogenic siloxanes **5**, **6**, and **7** as a function of temperature.

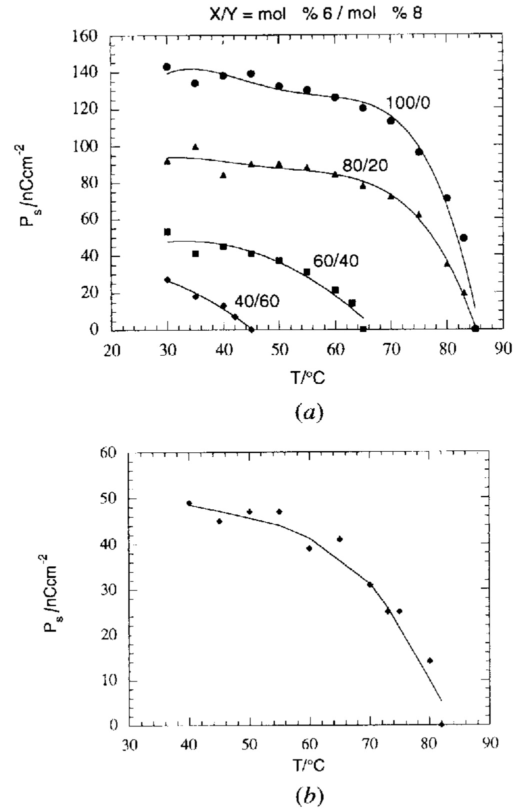
Thus the stabilizing influence of the siloxane backbone for smectic phases in the copolymers as well as in the dimesogenic mixtures becomes obvious.

To sum up, a pronounced similarity in phase behaviour can be discovered between the side group copolymers and dimesogenic siloxanes, while mixtures of the corresponding low molar mass precursors show significantly different phase sequences.

4. Ferroelectric properties

The spontaneous polarizations of the materials showing a S_C^* phase were measured. The results are shown in figure 4. The dimesogenic oligosiloxanes **6** and **7** can be switched at room temperature. The switching time of **6** is 45 μs (85°C) and material **7** has a switching time of 30 μs at 38°C. These values are significantly faster than those of typical polymers (some ms). In oligosiloxane derivative **5**, the S_C^* phase is frozen in at room temperature, and this may be interesting for storage processes. **5** has a transition from the S_C^* phase directly to the isotropic phase, and therefore the spontaneous polarization does not strongly depend on the temperature.

Again, a comparison of the dimesogenic siloxane mixtures and the copolymers is of interest. In the case of the copolymer systems, the spontaneous polarization could only be measured for one copolymer. In contrast, a number of different mixtures could be investigated. Here we have another hint of the positive influence of the higher fluidity of these systems. However, looking at the qualitative results, one can again recognize a distinct similarity between the two systems. This is clarified in figure 5, where the spontaneous polarizations of both systems are shown as a function of temperature.



(*a*)

(*b*)

Figure 5. Spontaneous polarizations of (*a*) mixtures of the dimesogenic siloxanes **6** and **8**, and (*b*) of copolymer **P4** as a function of temperature.

5. Experimental

Starting materials for the syntheses were obtained from Aldrich Chemie GmbH. The siloxanes and the catalyst for the hydrosilylation reaction were a gift from Wacker Chemie. The oligosiloxane had a mean number of repeat units *n* of 7. It is a polydisperse material with *n* ranging from 3 to 18.

5.1. *Synthesis of ethyl 4-(but-3-enyloxy)benzoate*

3·0 g of ethyl 4-hydroxybenzoate (18 mmol) and 2·7 g of 4-bromobut-l-ene (20 mmol) are dissolved in 88 ml of dry acetone. 7·9 g of K_2CO_3 are added together with a small portion of potassium iodide. The mixture is heated under reflux for 5 days. After cooling, the inorganic salts are filtered off and the solvent is evaporated. The crude product is purified by flash chromatography. Eluent: dichloromethane. Yield: 1·05 g (26·5 per cent). ^{1}H NMR (90 MHz, $CDCl_3$), δ [ppm]: 7·8 (d, 2 H, aromat. H), 6·7 (d, 2 H, aromat. H), 5·8 (m, 1 H, $CH_2{=}\underline{CH}{-}(CH_2)_2{-}O{-}$), 4·95 (m, 2 H, $\underline{CH_2}{=}CH{-}(CH_2)_2{-}O{-}$), 4·1 (q, 2 H, $-COO-\underline{CH_2}-CH_3$), 3·8 (t, 2 H, $CH_2{=}CH{-}CH_2{-}\underline{CH_2}{-}O{-}$), 2·3 (q, 2 H, $CH_2{=}CH{-}\underline{CH_2}{-}CH_2{-}O{-}$), 1·15 (t, 3 H, $-COO-CH_2-\underline{CH_3}$).

5.2. *Synthesis of 4-(but-3-enyloxy)benzoic acid*

1·05 g of ethyl 4-(but-3-enyloxy)benzoate (4·8 mmol) are dissolved in 25 ml of ethanol and 0·56 g of potassium hydroxide is added. The mixture is heated under reflux for 3 h. After cooling, 25 ml of 5 M aqueous HCl are added. The precipitated product is filtered off and dried. It is pure enough for further reactions. Yield: 830 mg (90·6 per cent); m.p. 128·5°C. ^{1}H NMR (90 MHz, $CDCl_3$), δ [ppm]: 8·0 (d, 2 H, aromat. H), 6·85 (d, 2 H, aromat. H), 5·8 (m, 1 H, $CH_2=C\underline{H}-(CH_2)_2-O-$), 5·0 (m, 2 H, $C\underline{H}_2=CH-(CH_2)_2-O-$), 4·0 (t, 2 H, $CH_2=CH-CH_2-C\underline{H}_2-O-$), 2·5 (q, 2 H, $CH_2=CH-C\underline{H}_2-CH_2-O-$).

5.3 *Synthesis of cholesteryl 4-(but-3-enyloxy)benzoate*

620 mg of 4-(but-3-enyloxy)benzoic acid (3·2 mmol) and 1250 mg of cholesterol (3·2 mmol) are dissolved in 20 ml of dry THF and cooled to 0°C. Then 666 mg (3·2 mmol) of dicyclohexylcarbodiimide are added in 20 ml of dry CH_2Cl_2. The mixture is stirred at 0°C for 4 h and then overnight at ambient temperature. After this the precipitated dicyclohexylurea is filtered off and the solvent is evaporated. The remaining solid is purified by flash chromatography, using CH_2Cl_2 as eluent. Yield: 750 mg (41·8 per cent). Phase transitions: C 119 N* 226 I. ^{1}H NMR (90 MHz, $CDCl_3$), δ [ppm]: 7·9 (d, 2 H, aromat. H), 6·8 (d, 2 H, aromat. H), 5·8 (m, 1 H, $CH_2=C\underline{H}-(CH_2)_2-O-$), 5·3 (m, 1 H, $=C-\underline{H}$ of cholesterol), 5·0 (m, 2 H, $C\underline{H}_2=CH-(CH_2)_2-(O-$), 4·0 (t, 2 H, $CH_2=CH-CH_2-C\underline{H}_2-O-$), 2·5 (q, 2 H, $CH_2=CH-C\underline{H}_2-CH_2-O-$), 2·2–0·5 (several m, 34 H, aliphatic H of cholesterol).

5.4. *Preparation of the dimesogenic LC oligosiloxanes (general procedure)*

Typically 2·9 mmol of alkene precursor (**1–4**) and 795 mg (1·4 mmol) of the Si–H containing oligomeric siloxane are dissolved in 18 ml of dry toluene and 2 ml of a solution of 1·0 mg of dichlorodicyclopentadienyl-platinum in 10 ml of dry toluene are added. The reaction mixture is degassed and then stirred for 24 h at 100°C in a nitrogen atmosphere. Then another 2 ml of the platinum catalyst solution are added and the reaction mixture is stirred for another 24 h at 100°C. Afterwards the solvent is removed and the crude product is purified by flash chromatography.

Details for the four LC oligosiloxanes (**5–8**) are given below:

5: Eluent: toluene; Yield: 71·3 per cent. ^{1}H NMR (200 MHz, $CDCl_3$), δ [ppm]: 8·3–6·8 (several m, 24 H, aromat. H), 4·4 (m, 2 H, $CH_3-CH_2-C\underline{H}^*(CH_3)-O-$), 4·0 (t, 4 H, $-(CH_2)_{10}-C\underline{H}_2-O-$), 2·2–1·2 (several m, 46 H, $CH_3-C\underline{H}_2-CH^*(C\underline{H}_3)-O-$ and $O-CH_2-(C\underline{H}_2)_9-CH_2-$), 1·0 (t, 6 H, $C\underline{H}_3-CH_2-CH^*(CH_3)-O-$), 0·5 (t, 4 H, $O-Si-C\underline{H}_2-(CH_2)_{10}-O-$), 0·05 (s, 48 H, $O-Si-C\underline{H}_3$).

6: Eluent: toluene. Yield: 72·8 per cent. ^{1}H NMR (200 MHz, $CDCl_3$), δ [ppm]: 8·6–6·8 (several m, 22 H, aromat. H), 4·4 (m, 2 H, $CH_3-(CH_2)_5-C\underline{H}^*(CH_3)-O-$), 3·9 (t, 4 H, $-(CH_2)_{10}-C\underline{H}_2-O-$), 2·1–1·0 (several m, 62 H, $CH_3-(C\underline{H}_2)_5-CH^*(C\underline{H}_3)-O-$ and $O-CH_2-(C\underline{H}_2)_9-CH_2-$), 1·0 (t, 6 H, $C\underline{H}_3-CH_2-CH^*(CH_3)-O-$), 0·5 (t, 4 H, $O-Si-C\underline{H}_2-(CH_2)_{10}-O-$), 0·05 (s, 48 H, $O-Si-C\underline{H}_3$).

7: Eluent: CH_2Cl_2. Yield: 77·4 per cent. ^{1}H NMR (200 MHz, $CDCl_3$), δ [ppm]: 8·1–7·0 (several m, 16 H, aromat. H), 4·4 (d, 2 H, $-C\underline{H}^*(Cl)-CH^*(CH_3)-C_2H_5$), 4·1 (t, 4 H, $-(CH_2)_9-C\underline{H}_2-O-$), 2·2 (m, 2 H, $-CH^*(Cl)-C\underline{H}^*(CH_3)-C_2H_5$), 1·9–1·6 (m, 4 H, $-CH^*(CH_3)-C\underline{H}_2-CH_3$), 1·5–1·2 (m, 36 H, $-O-Si-CH_2-(C\underline{H}_2)_9-CH_2-O-$), 1·15 (d, 6 H, $-CH^*(Cl)-CH^*(C\underline{H}_3)-C_2H_5$), 1·0 (t, 6 H, $-CH^*(CH_3)-CH_2-C\underline{H}_3$), 0·5 (t, 4 H, $O-Si-C\underline{H}_2-(CH_2)_{10}-O-$), 0·05 (s, 48 H, $O-Si-C\underline{H}_3$).

8: Eluent: CH_2Cl_2. Yield: 91·4 per cent. ^{1}H NMR (200 MHz, $CDCl_3$), δ [ppm]: 7·9 (d, 4 H, aromat. H), 6·8 (d, 4 H, aromat. H), 5·3 (m, 2 H, $=C-\underline{H}$ of cholesterol), 4·0 (t, 4 H, $-(CH_2)_3-C\underline{H}_2-O-$), 2·4 (m, 2 H, $-(CH_2)_2-C\underline{H}_2-CH_2-O-$), 2·1–0·5 (several m, 72 H, aliphatic H of cholesterol and $Si-C\underline{H}_2-(CH_2)_3-$), 0·05 (s, 48 H, $O-Si-C\underline{H}_3$).

The polymers were prepared according to [6]. The composition of the copolymers was checked by ^{1}H NMR (200 MHz). For this purpose, signals of different aromatic protons were used. They were separated from each other and could be assigned to the different mesogenic moieties. The composition of the copolymers was in agreement with the feed stock of starting materials in the reaction mixture.

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