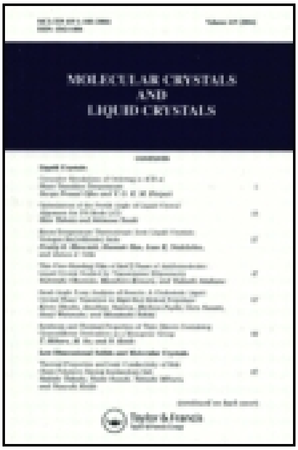

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Cyclic Siloxanes With Mesogenic Side Groups

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Cyclic Siloxanes with Mesogenic Side Groups

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(Received August 20, 1990)

Cyclic liquid crystalline siloxanes (CLCS) are optical uniaxial positive (S_A, N) and negative (N*) materials in accordance with calamitic structures. X-Ray measurements indicate, that the distances of S_A layers correspond with the length of the monomer unit. In the case of mesogens with high polarity the distance is 1.7 fold the length of the monomer unit. A bundle model is proposed for CLC siloxanes.

1. INTRODUCTION

The first cyclic liquid crystalline side chain siloxanes (CLCS) were synthesized in 1981.[1-2] Some of these materials especially cholesterics were examined by several groups.[3-11] In the meantime further examples were published[12] and compared with their linear analogues. The structures of the phases are discussed to be discotic[13,14] or calamitic. In this study different series of CLCS (homo- and copolymers) with oxygen containing and oxygen free spacers were synthesized to outline the calamitic character of the CLCS.

2. EXPERIMENTAL

2.1 General Procedures

^{1}H-NMR and ^{29}Si-NMR spectra were recorded on a Bruker WP 200 SY NMR spectrometer.

For optical observations a Zeiss Orthoplan polarizing microscope equipped with a Mettler hot stage FP 82 was used.

DSC scans were recorded on a Mettler TA 3000.

X-Ray powder diffraction patterns were obtained using a Siemens diffractometer D 500. For small angle observations additional a Kratky camera (Paar) was used.

THF was dried over Na. The other solvents and reagents of reagent grade quality were used as received without further purification.

The hydrogen containing cyclic siloxanes with 3–7 Si atoms were prepared according to References 15 and 16 and methyl-vinyl cyclosiloxanes according to

References 17 and 18. The synthesis of mesogenic groups with oxygen containing spacers is well known.[19] Dimethylsilylbenzoic acid chlorides were synthesized according to Reference 20. The hydrosilylation reactions were carried out in toluene at 60–111°C by using dicyclopentadienyl-Pt-dichloride as catalyst.[2,21]

Modeling of the CLCS structures and the calculation of the lengths of the mesogenic groups were done by means of the programs INSIGHT and DISCOVER (Molecular Modeling System, Vers. 2.5, BIOSYM Technologies, San Diego, CA).

2.2 General Synthesis of Mesogenic Groups with Oxygen Free Spacers

a) ω-Alkenyl-4-chlorobenzenes. 2.05 Mol Mg is submerged in a small amount of THF and heated up to 80°C in an inert atmosphere. By addition of 10 ml of a solution of 2 Mol 1.4-dichlorobenzene in 500 ml dry THF the Grignard reaction starts. The rest of the solution is added under stirring during 2 h at 80°C. After 2 h the Grignard solution is separated from excess of Mg and mixed with 1.8 Mol of 1-bromo-ω-alkene. The reaction is completed by refluxing for 15 h. After pouring on ice the mixture is acidified, the organic phase separated, dried, and fractionated (Table I).

b) 4-(ω-Alkenyl)benzoic acids. To 2.2 Mol Mg a mixture of 1.85 Mol 4-(ω-alkenyl)-1-chlorobenzene in 500 ml THF and 2 ml ethyliodine is added during 5 h maintaining the temperature at 83°C. Then the mixture is refluxed for 3 h and stirred overnight. After separation from the remaining Mg the solution is mixed at 5–15°C with 500 ml CO_2 saturated THF. During this procedure additional CO_2 is bubbled through the mixture. After 30 min. the solution is poured on ice and

TABLE I

Physical properties of ω-alkenyl-4-chlorobenzenes and 4-(ω-alkenyl)benzoic acids $H_2C{=}CH(CH_2)_{(a-2)}C_6H_4\text{-}X$

Nr.	a	X	b.p.(°C)[1]	Phase transition (°C)
01	3	Cl	66-68	
02	3	COOH		C 98 N 122 I
03	4	Cl	84	
05	4	COOH		C 117 N 130 I
06	5	Cl	105-107	
07	5	COOH		C 76 N 96 I
08	6	Cl	116-118	
09	6	COOH		C 84 N 117 I

[1] b.p. at 13 mbar.

acidified with 200 ml HCl. The phases are separated and the alkenyl-benzoic acid is recrystallized from heptane (Table 1). The esters are made by standard methods.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The best method to obtain CLCS is the hydrosilylation of well defined SiH cycles (Figure 1) with ω-unsaturated mesogens. In the case of allyloxy derivatives the hydrosilylation is accompanied by a remarkable side reaction, characterized by splitting the CO-bond of the allyloxy group, propene elimination and direct attack of silicon to the oxygen.[22] This is an additional complication of the difficult purification of LC-siloxanes.[23,24] Nevertheless mesogens containing allyloxy groups yield linear LC-siloxanes and CLCS with phases of sufficient stability using an unexpensive spacer.

Figure 2 shows the more complicated ^{1}H-NMR spectrum of the reaction mixture after the hydrosilylation of an allyloxyderivative in comparison with the corresponding butenylderivative: due to the direct connection of the silicon atom to the oxygen of the benzoic ester part of the molecule the aromatic signals of the regular product are superimposed by these signals. In addition the integrals of the CH_2-protons do not correspond to the integrals of the aromatic protons. Further the signals of the Si-CH_3-protons are accompanied by a second signal shifted 0.25 ppm to lower fields indicating H_3C-$SiO_{3/2}$-groups. The problems concerning the purification of the hydrosilylation products of allyloxyderivatives could be overcome by synthesizing the corresponding dichlorosilanes and their succeeding hydrolysis in high dilution. By theoretical and practical means it is not possible to obtain CLCS of definite ring sizes by this method without a separation procedure. Figure 3 shows the sharp signal at -22.6 ppm in the ^{29}Si-NMR spectrum of a hexenylderivative (a) and the splitted signals of a hydrolysate of a hexenylderivative indicating a mixture of different compounds (b).

3.2 Possible Structures

A glance to the formula of a CLCS associates the similarity to discotic liquid crystals (Figure 4). But another arrangement should also be considered. Despite the fact that the mesogenic substituents probably are statistically distributed in equatorial and axial positions of the siloxane ring a bundle model (Figures 5 and 6) explains the following optical observations. This model can also be applied to double ring systems (Liquid crystalline silsesquioxanes).

3.3 Optical Observations

The appearance of the phases of CLCS on the polarizing microscope are very similar or identical with the phases obtained from calamitic low molecular weight liquid crystals or polymeric materials (Figures 7–10).

The crucial experiment to distinguish nematic calamitic and discotic phases is a conoscopic determination of the crystallographic behaviour. A homeotropic ori-

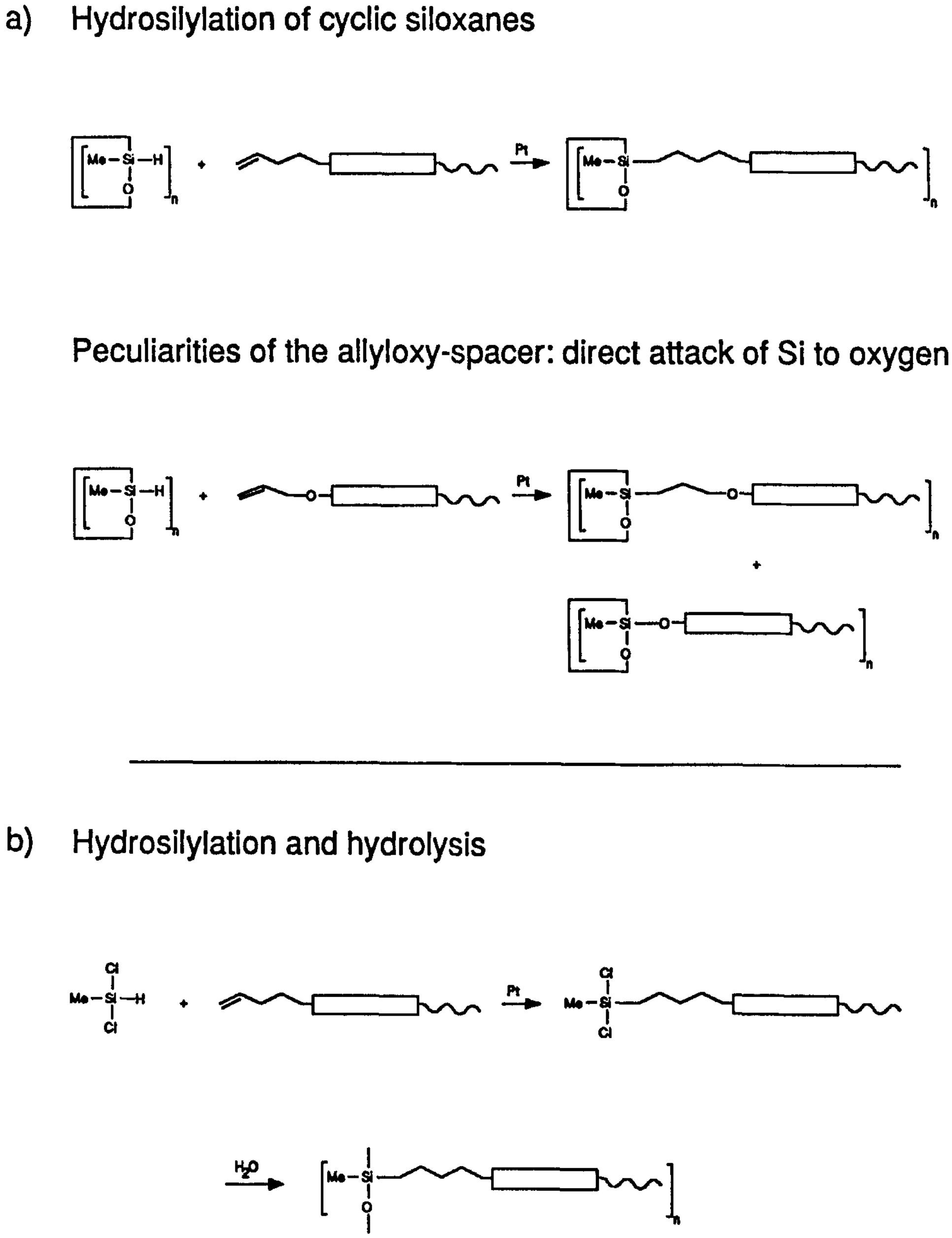


FIGURE 1 Reaction routes to obtain CLCS: Hydrosilylation of mesogenic olefins with a) cyclic hydrogensiloxanes, b) dichlorosilane and hydrolysis.

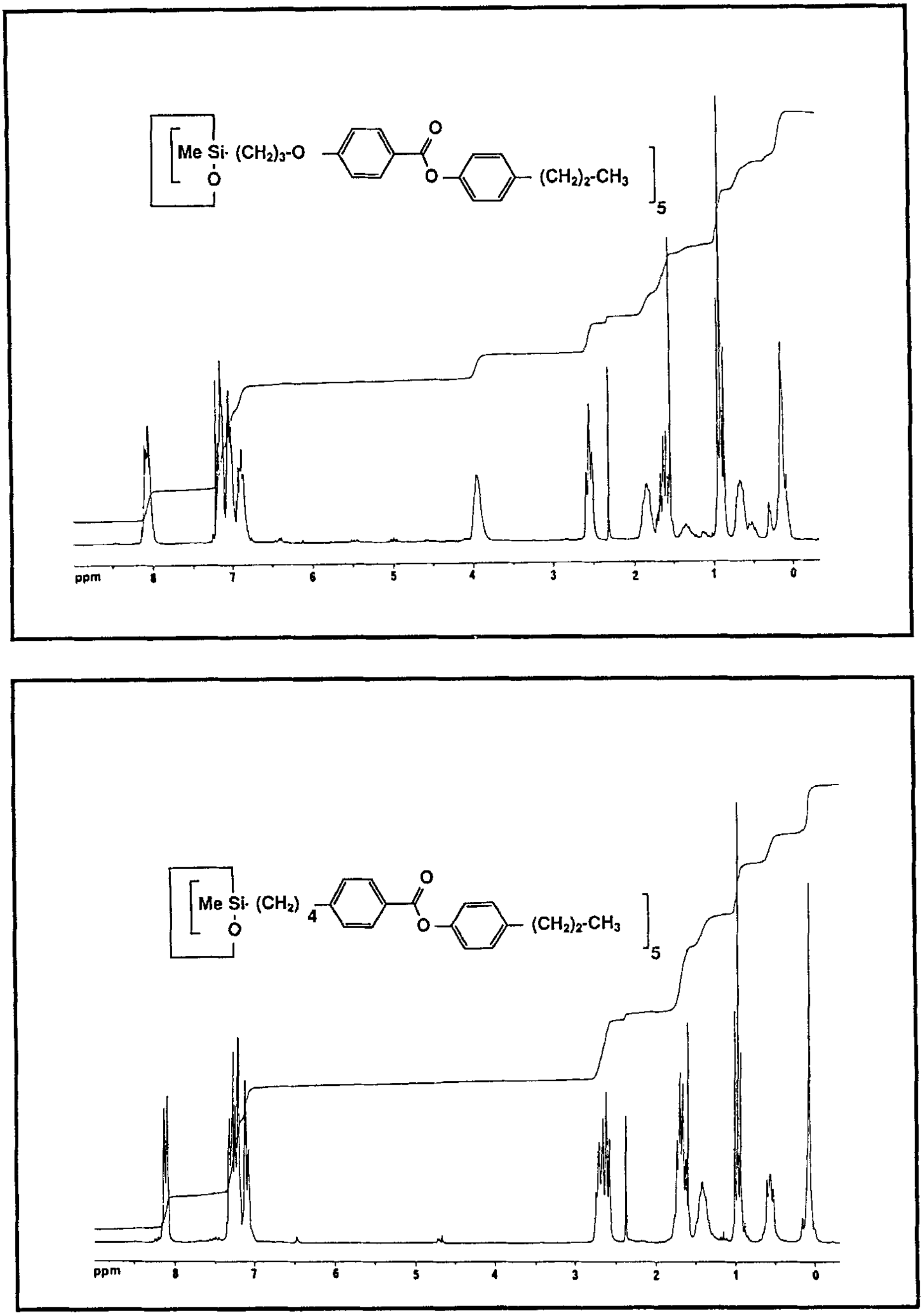


FIGURE 2 ^{1}H-NMR spectra of CLC-siloxanes. The addition of SiH to allyloxyderivatives is accompanied by evolution of propene and direct attack of the silicon atom to oxygen in contrast to the corresponding butenylderivative.

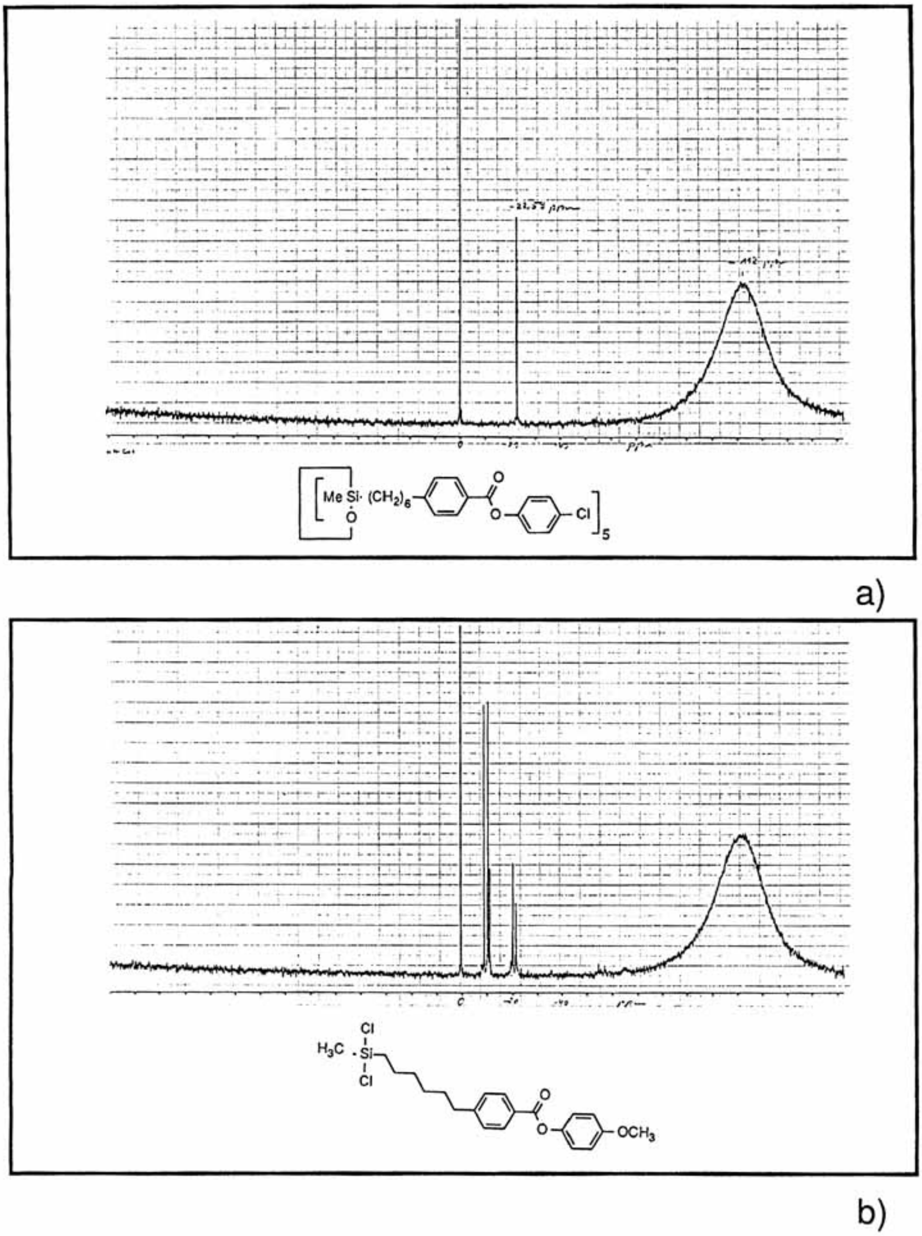


FIGURE 3 ^{29}Si-NMR spectra of CLC-siloxanes prepared a) by hydrosilylation of pentamethylcyclopentasiloxane, b) by hydrosilylation of methyldichlorosilane and succeeding hydrolysis.

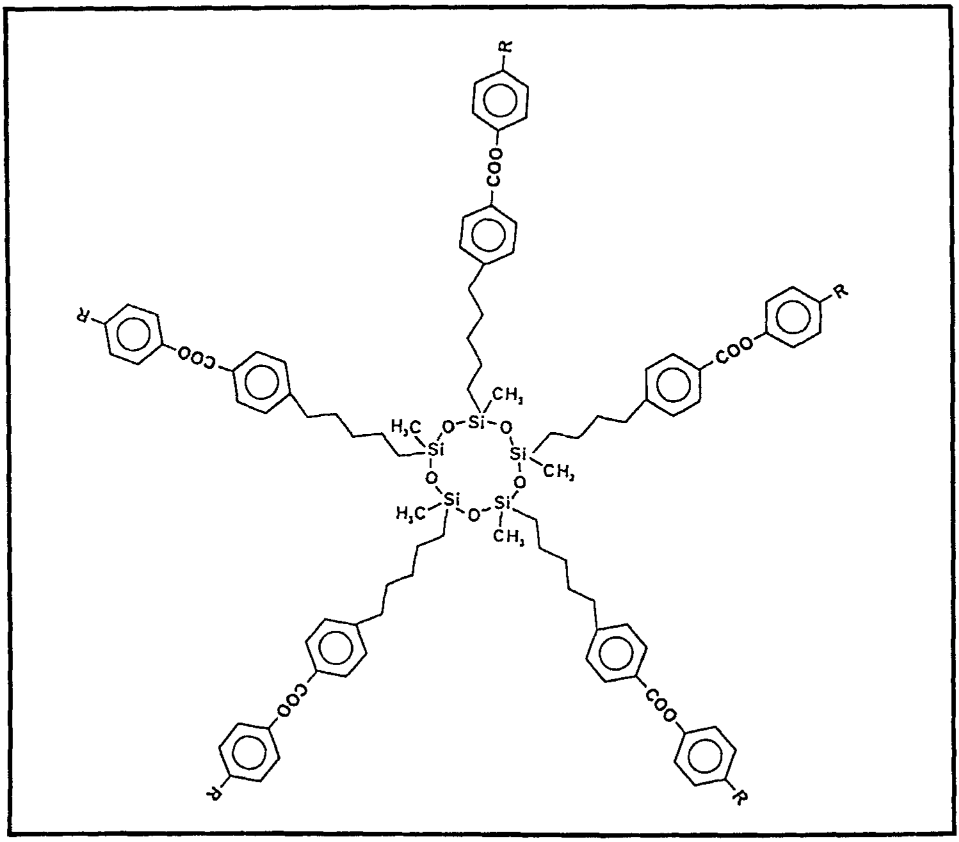


FIGURE 4 Formula of a cyclic LC-siloxane.

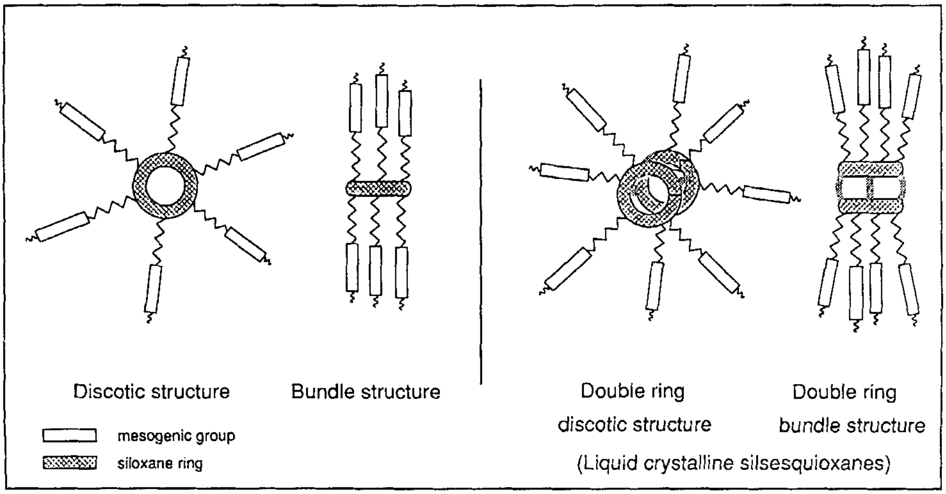


FIGURE 5 Possible planar and bundle structures of CLC-siloxanes of single ring systems and double ring systems (Liquid crystalline silsesquioxanes).

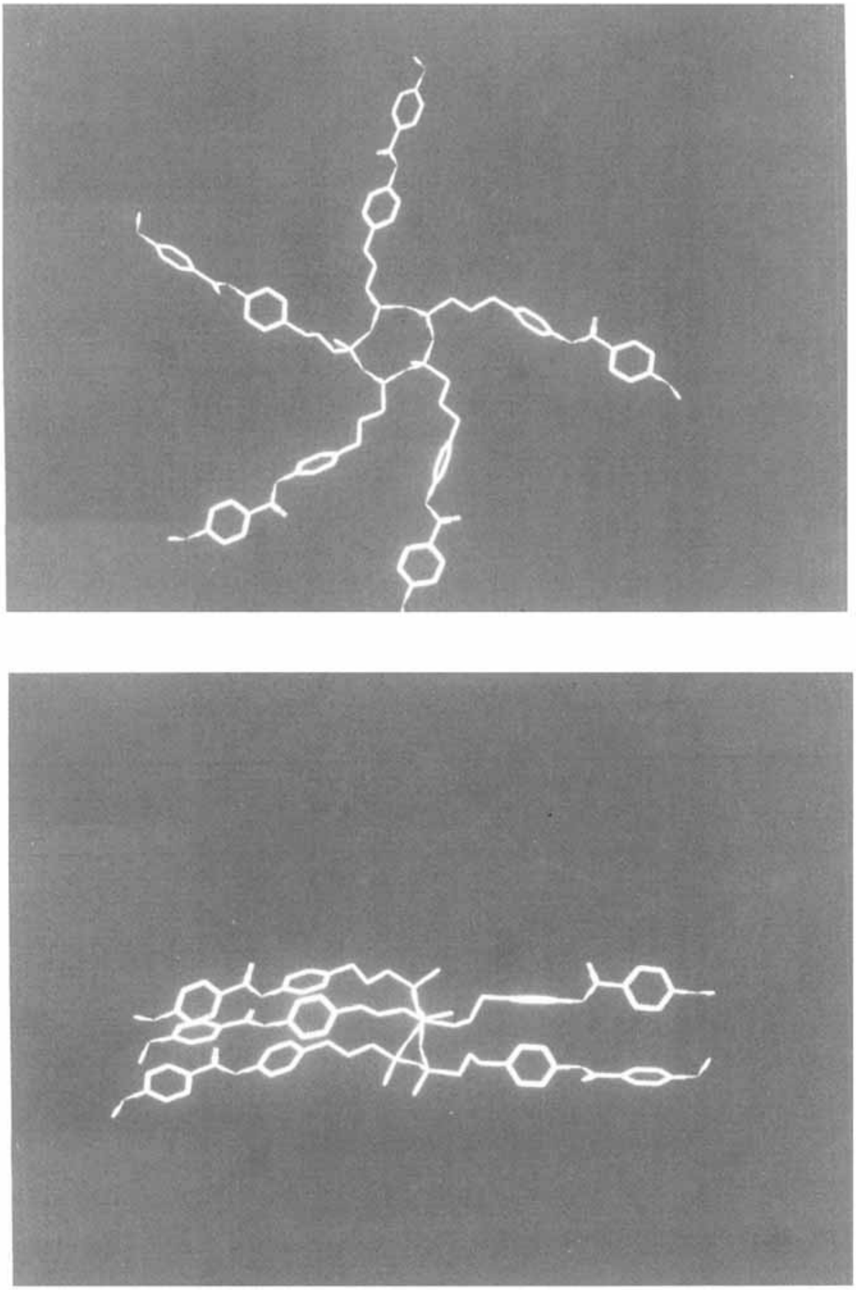


FIGURE 6 Computer simulations of CLC-siloxanes for the planar and bundle structure. See Color Plate XXVI.

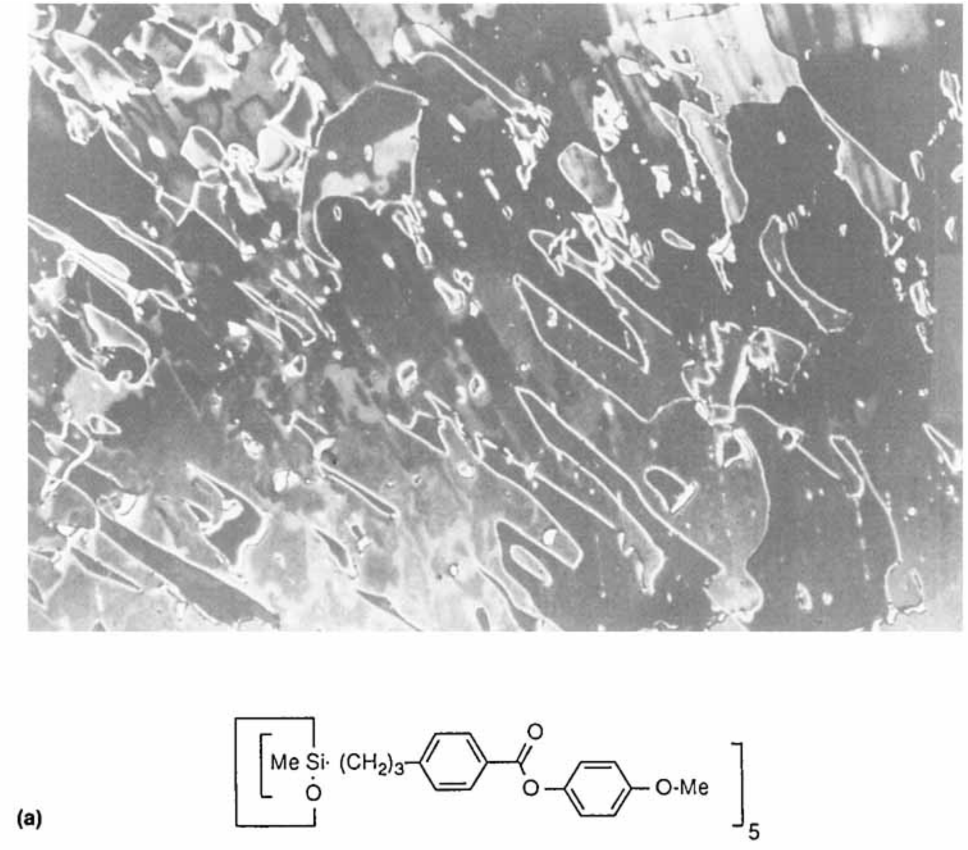


FIGURE 7 Nematic phases of **21** (a) and **27** (b). See Color Plate XXVII.

ented calamitic nematic sample should have a positive crystallographic axis, a discotic a negative one.[25] Nematic and smectic (A, B, E) CLCS exhibit positive axiality so they are calamitics (Figures 11 and 12). Cholesteric materials have a negative axiality (Figure 13).

3.4 Properties

3.4.1 Influence of the ring size on T_g. The influence of the ring size on the phase behaviour of CLCS was studied earlier.[12] Our own observations, concerning Si rings up to seven Si atoms indicate, that the ring size should be considered in connection with the nature of the mesogenic groups. Decreasing or increasing glass transition temperatures depend on the ring size, of course, but also on the molecular weight of the mesogenic groups (Figures 14–17). So in the case of moderate molecular weights of the mesogenic groups the glass transition temperatures decrease with increasing size of the cyclic siloxane backbone. By linking the siloxane ring

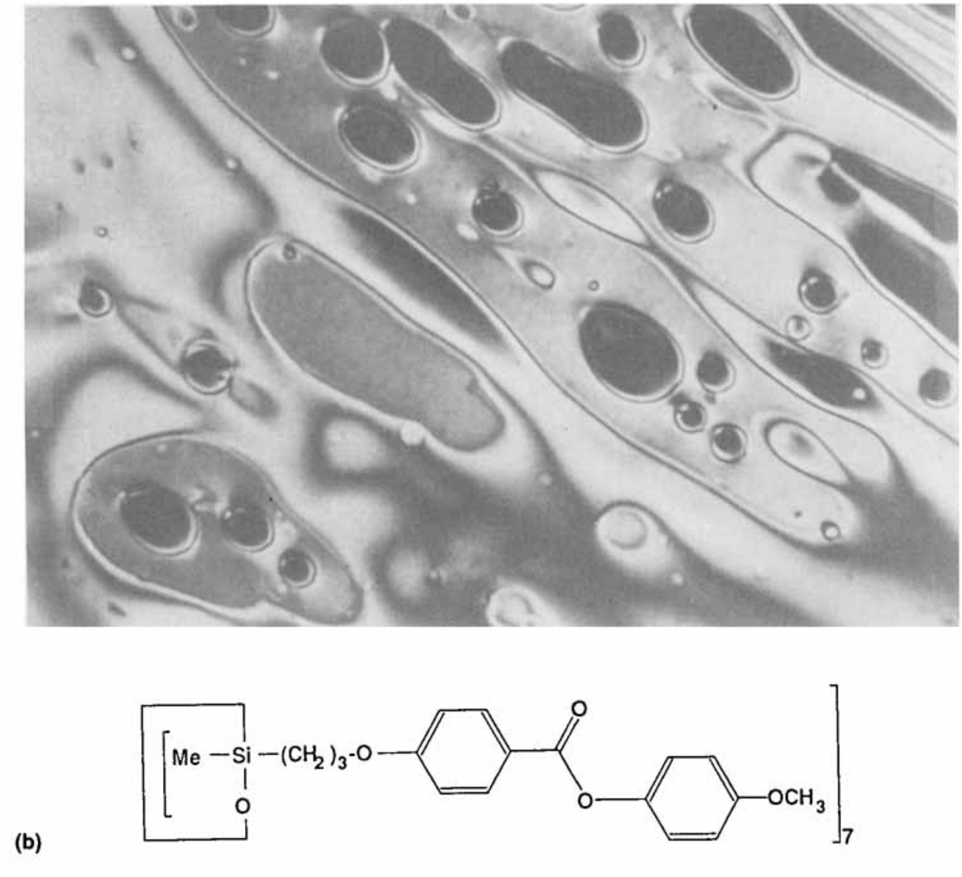


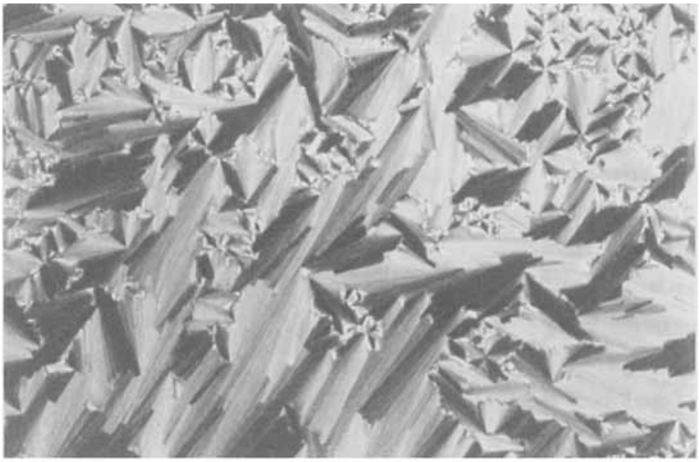
FIGURE 7b (*Continued*) See Color Plate XXVII.

to the heavy cholesteryl benzoate increasing glass transition temperatures are observed with increasing number of Si atoms in the siloxane ring (Figure 17).

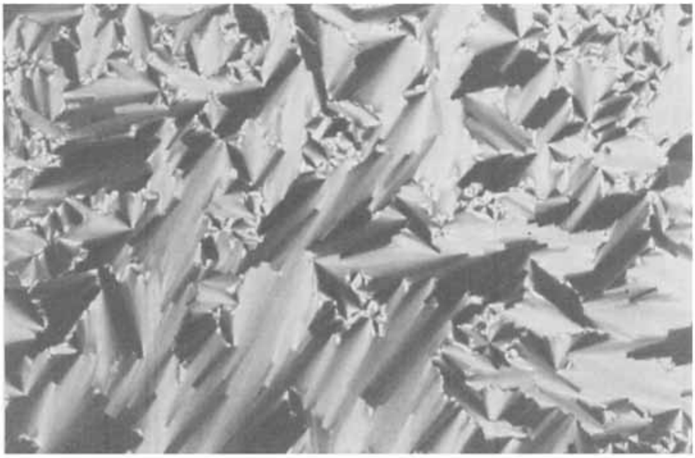
3.4.2 Influence of the spacer length on T_g. An increasing number of C atoms in the spacer length yields decreasing glass transition temperatures according to the linear LC siloxane series[26,27] (Figures 18–20). Also odd even effects may be observed.

3.4.3 Phase behaviour of copolymers. From the experimental conditions to synthesize statistical copolymers by hydrosilylation in the case of molecules with low degree of polymerization result molecules with different substitution patterns because the ratio of the monomer units is only defined for the reaction mixture. Therefore normally copolymeric CLCS consist of a mixture of different species with different composition and distribution of the monomer units.

The phase behaviour of such copolymers is influenced by the molar ratio of the



S_A 90°C



S_B RT

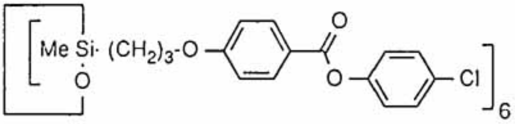


FIGURE 8 Smectic phases of **17**. Transition $S_A > S_B$. See Color Plate XXVIII.

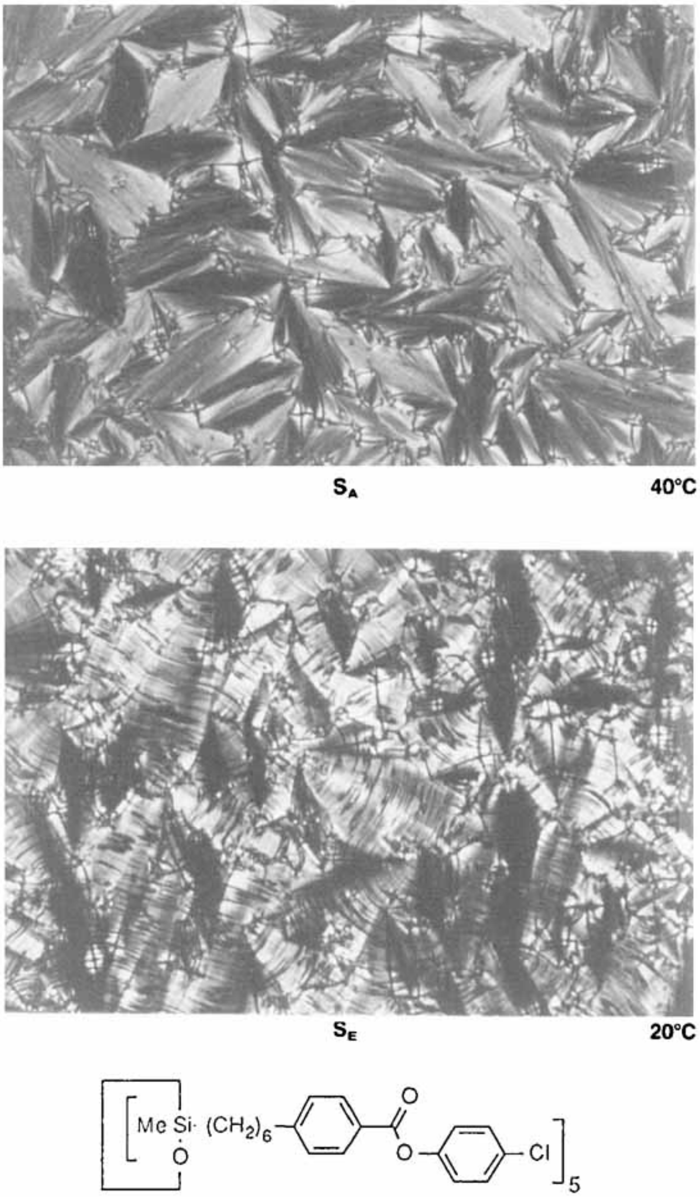


FIGURE 9 Smectic phases of **16**. Transition $S_A > S_E$. See Color Plate XXIX.

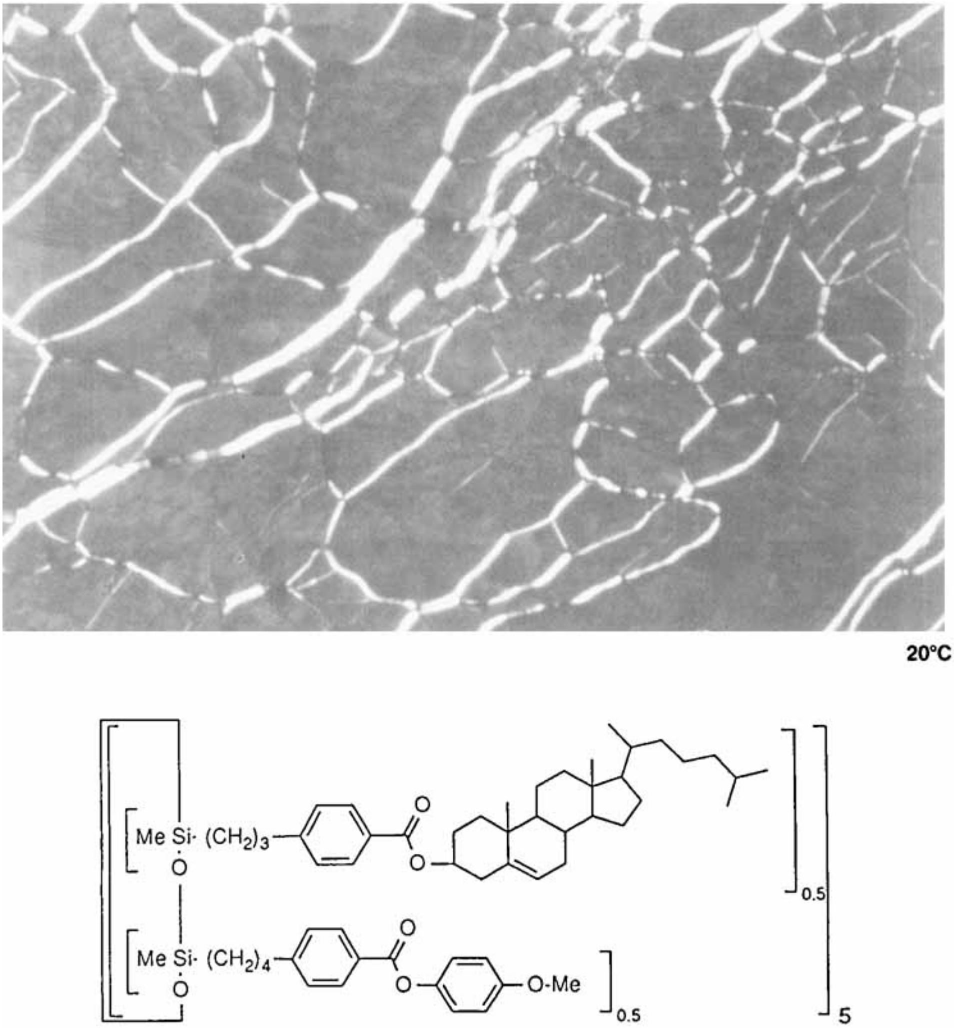


FIGURE 10 Grandjean texture of the cholesteric phase of **59**. See Color Plate XXX.

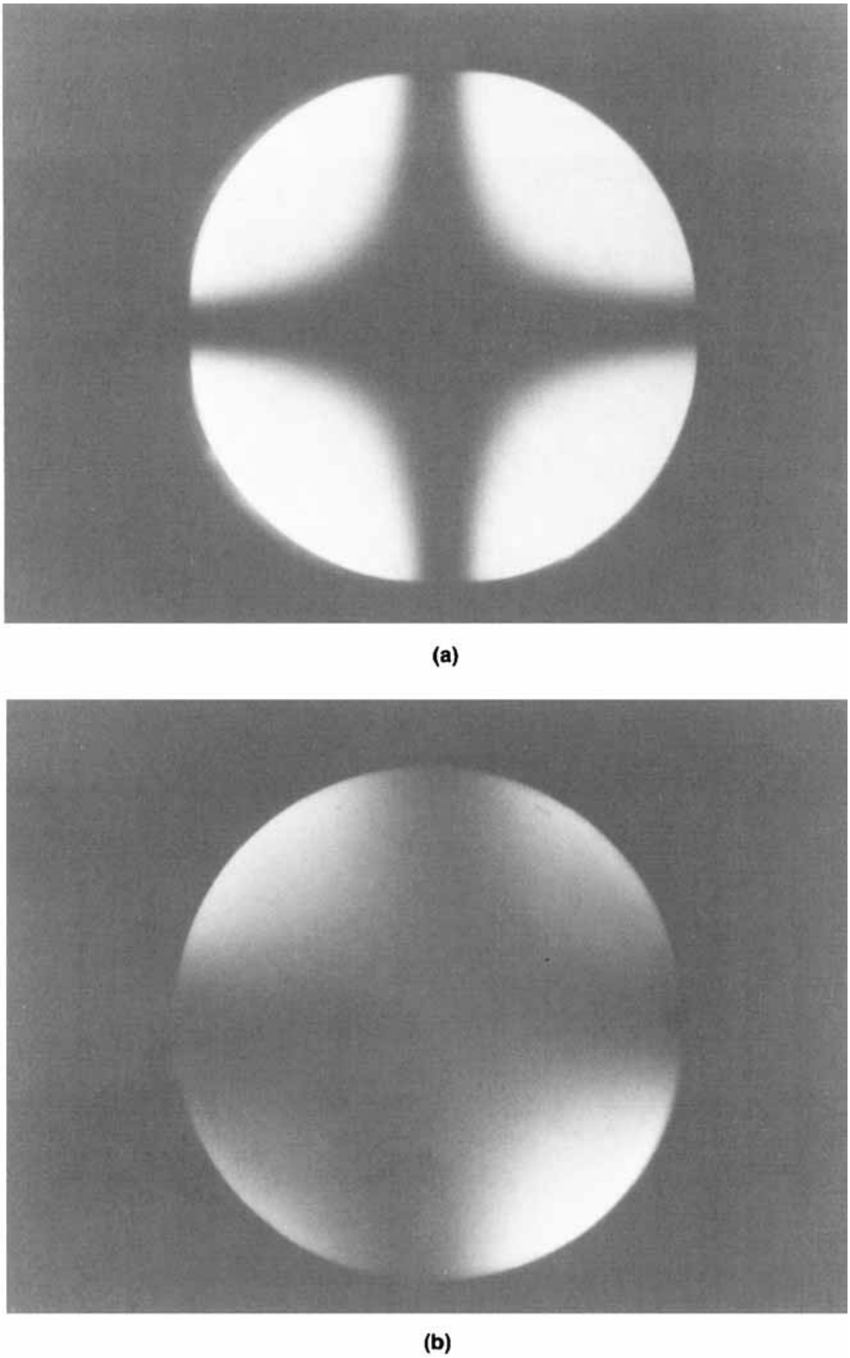
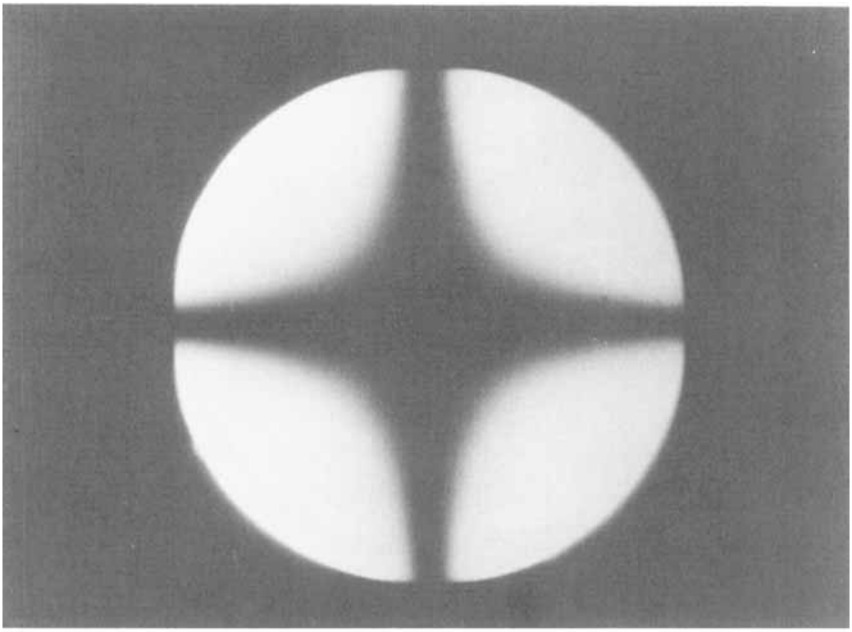
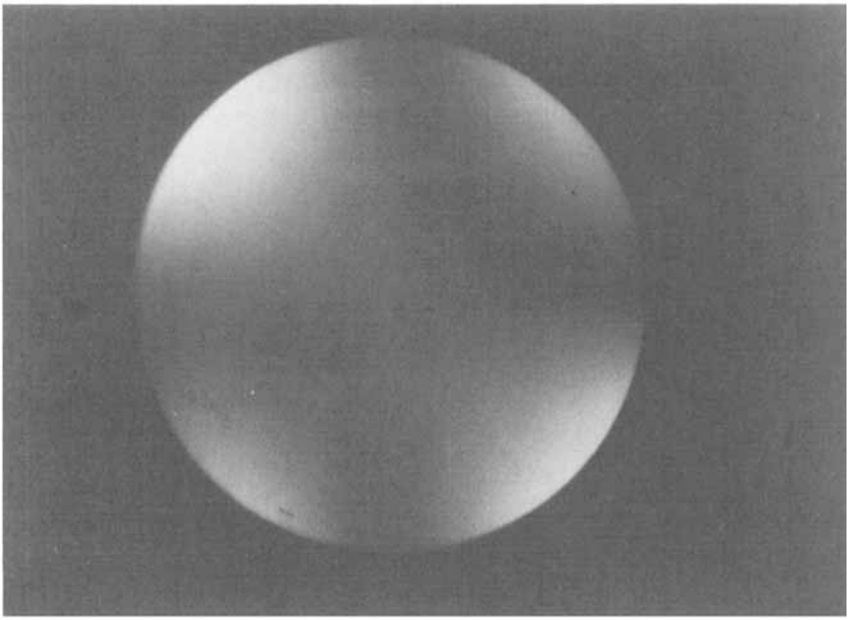


FIGURE 11 Conoscopic observation of the nematic phase of **21**. a) Microphotography of the homeotropic oriented phase. b) Observation with the compensator. The preparation exhibits a positive crystallographic axis. See Color Plate XXXI.

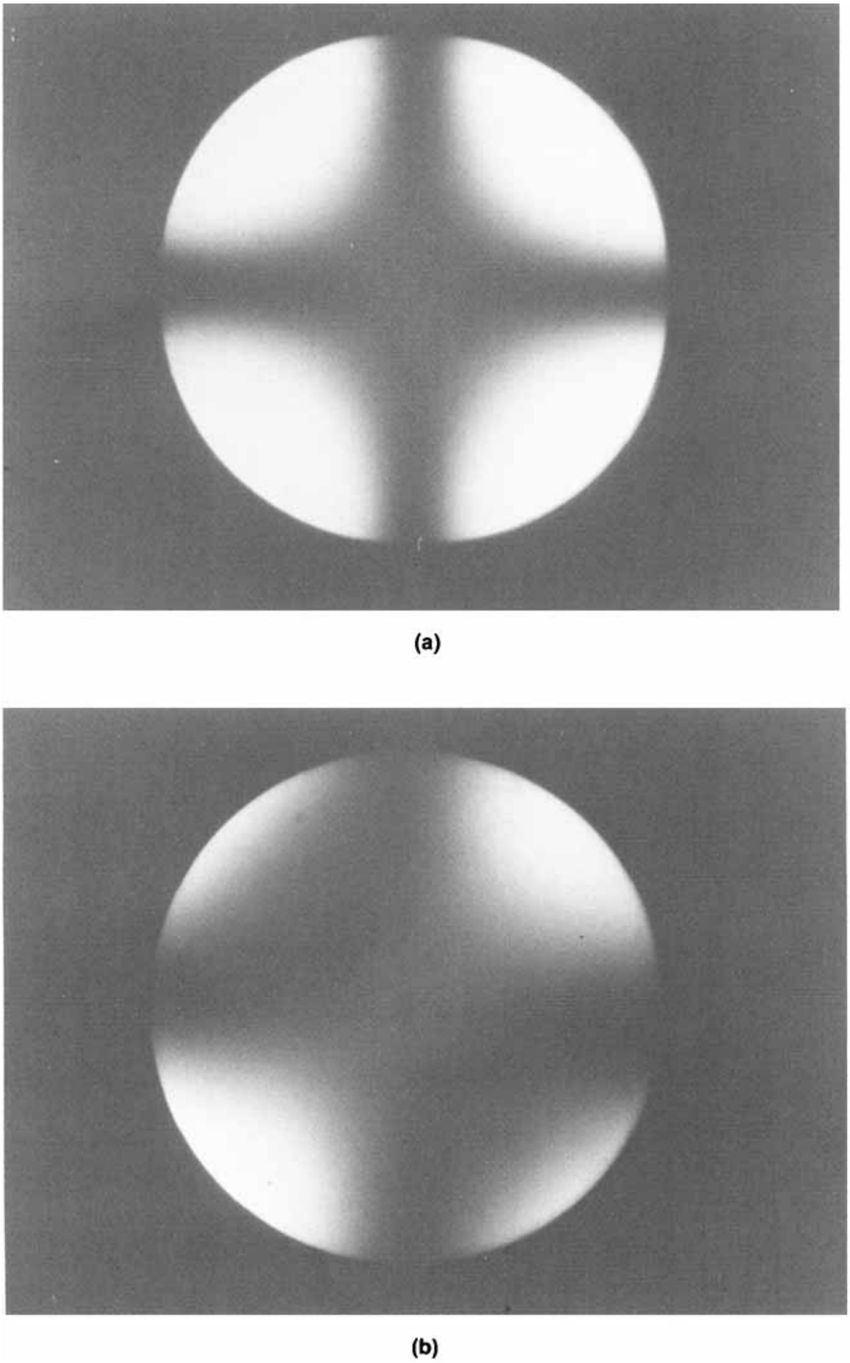


(a)



(b)

FIGURE 12 Conoscopic observation of the smectic A phase of **33**. a) Microphotography of the homeotropic oriented phase. b) Observation with the compensator. The preparation exhibits a positive crystallographic axis. See Color Plate XXXII.



(a)

(b)

FIGURE 13 Conoscopic observation of the cholesteric phase of **59**. a) Microphotography of the Grandjean texture. b) Observation with the compensator. The preparation exhibits a negative crystallographic axis. See Color Plate XXXIII.

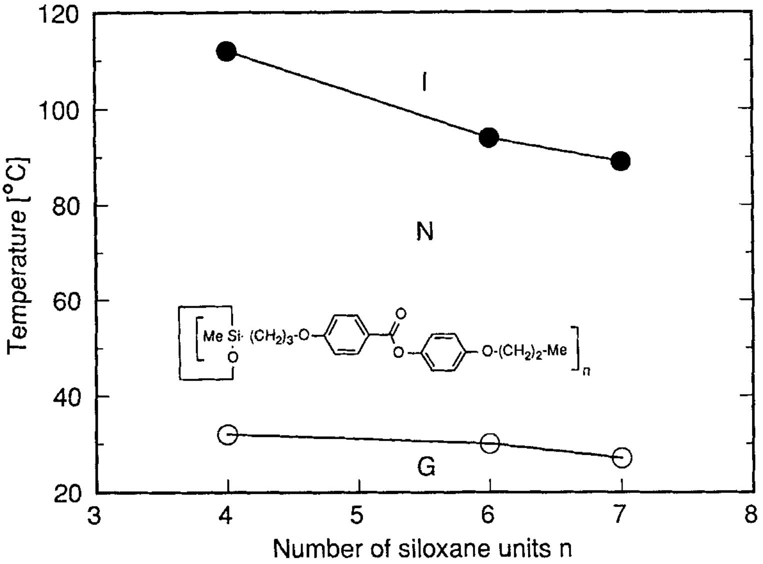


FIGURE 14 Influence of ring size on phase transition temperatures. With increasing size of the siloxane ring the glass transition temperature decreases.

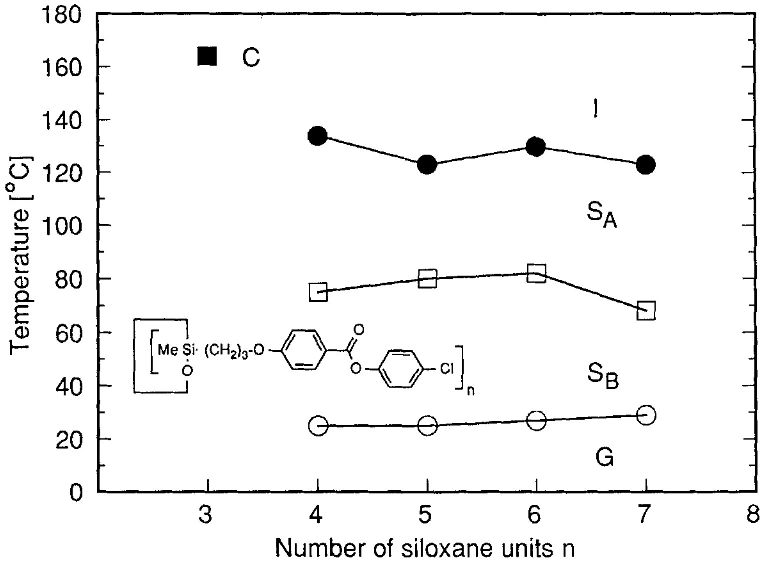


FIGURE 15 Influence of ring size on phase transition temperatures. The influence of the size of the siloxane ring on the glass transition temperature can be neglected.

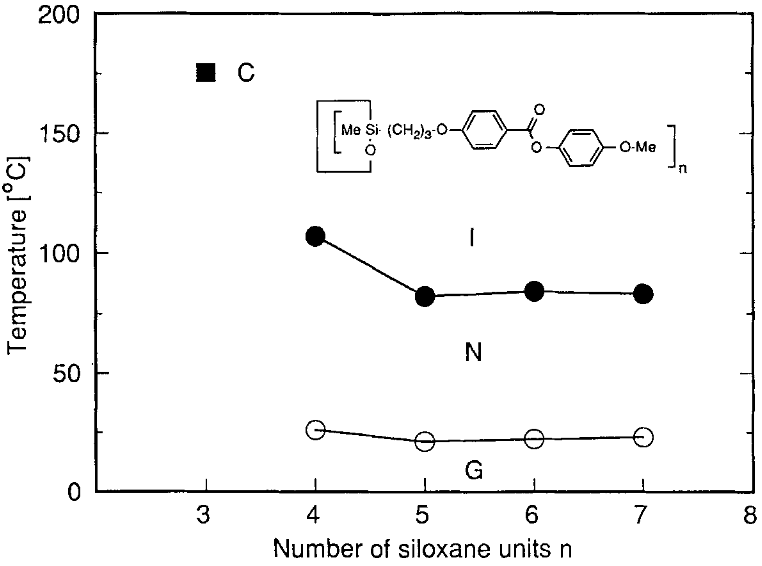


FIGURE 16 Influence of ring size on phase transition temperatures. The influence of the size of the siloxane ring on the glass transition temperature can be neglected.

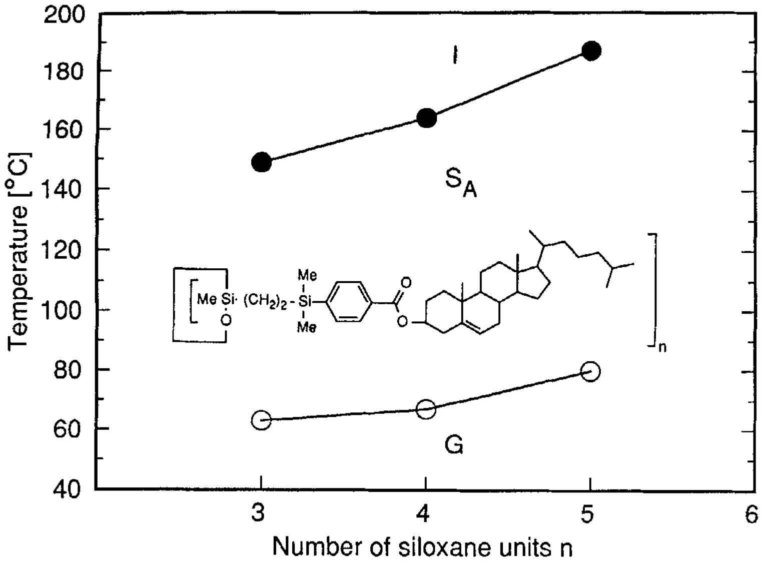


FIGURE 17 Influence of ring size on phase transition temperatures. With increasing size of the siloxane ring the glass transition temperature increases.

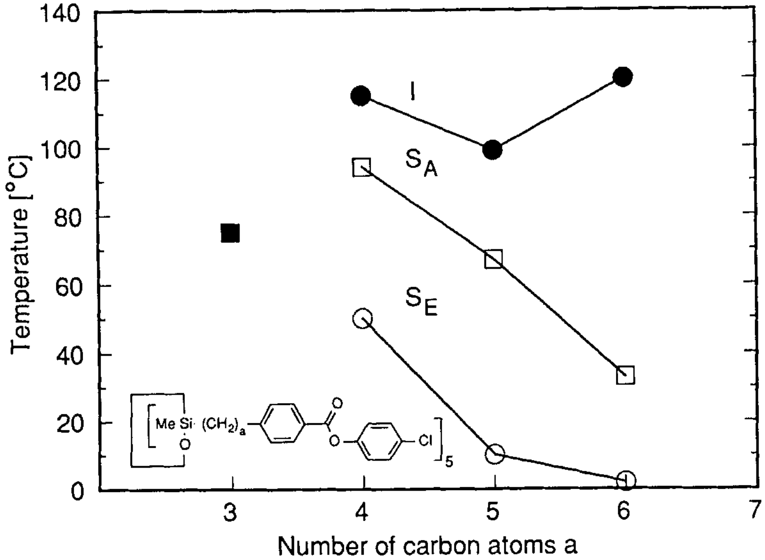


FIGURE 18 Influence of spacer length on phase transition temperatures. With increasing size of the spacer length the glass transition temperature decreases.

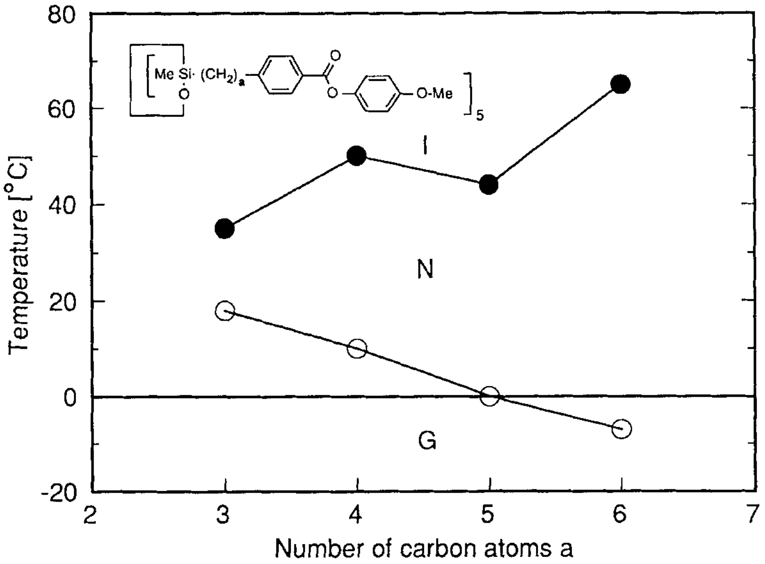


FIGURE 19 Influence of spacer length on phase transition temperatures. With increasing size of the spacer length the glass transition temperature decreases.

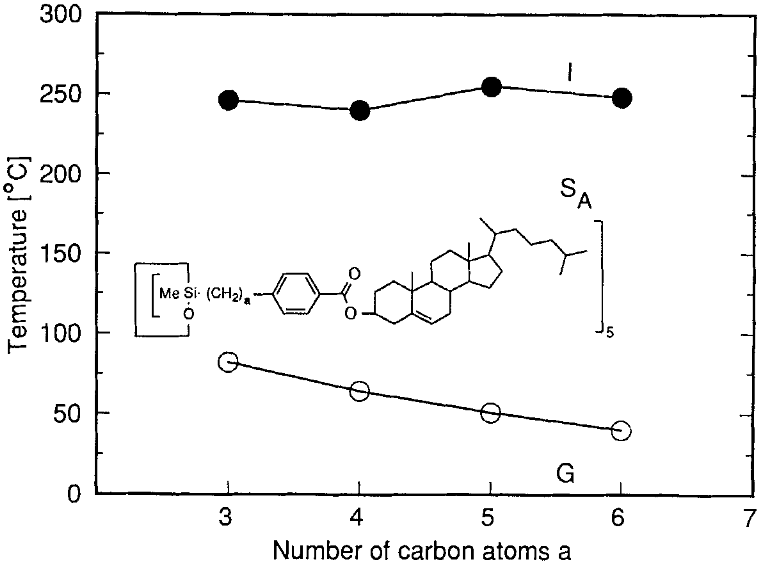


FIGURE 20 Influence of spacer length on phase transition temperatures. With increasing size of the spacer length the glass transition temperature decreases.

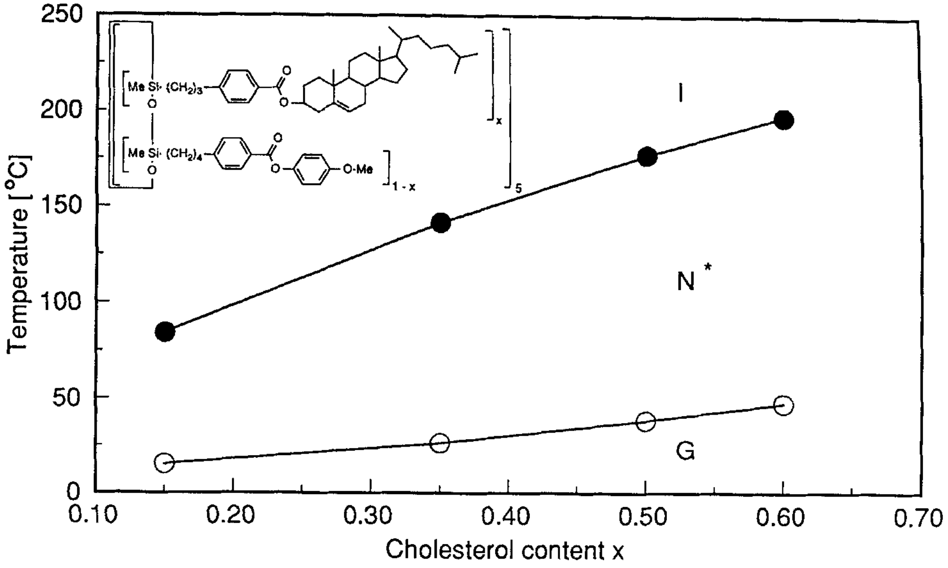


FIGURE 21 Influence of cholesterol content on glass transition and clearing temperature. With increasing content of cholesterol glass and clearing temperatures increase.

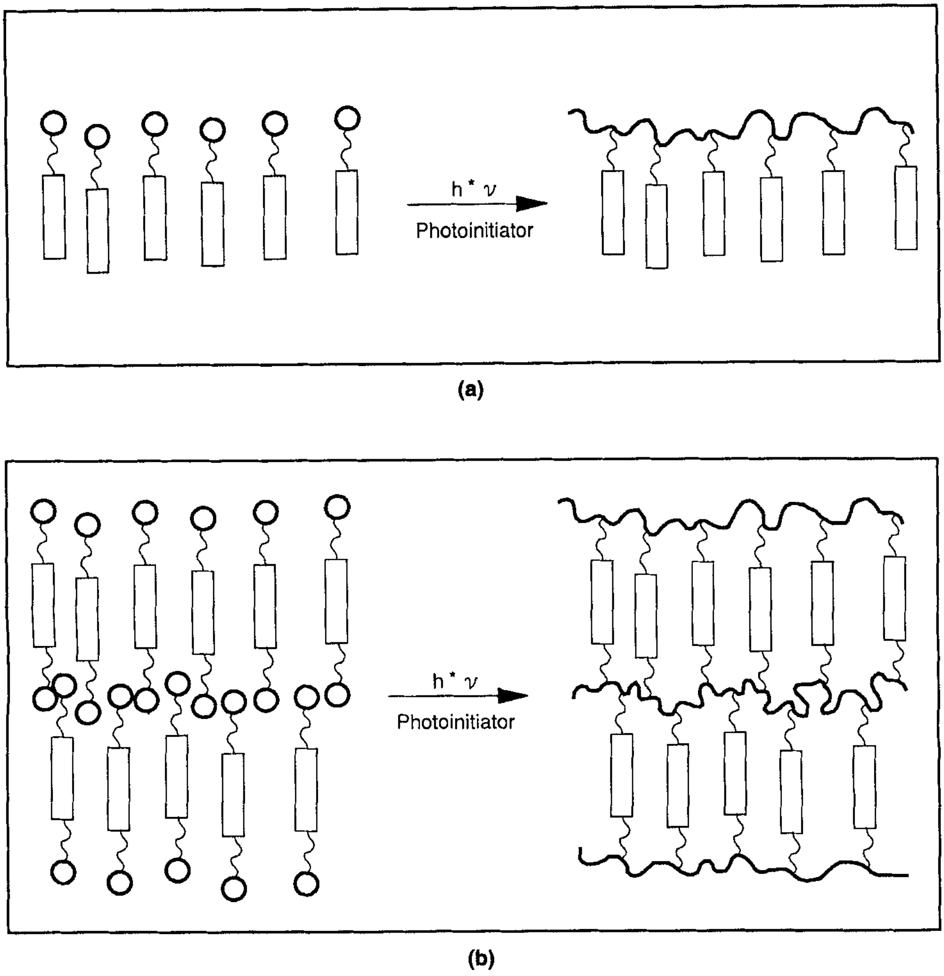


FIGURE 22 Cationic polymerization of CLC-siloxanes. a) Polymerization of a monosubstituted mesogenic group. b) Polymerization of a disubstituted mesogenic group.

TABLE II

Phase transitions of cyclic liquid crystalline siloxanes (CLCS)

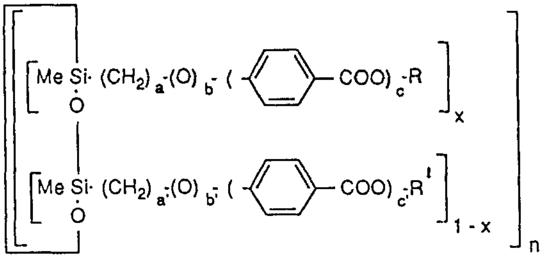


TABLE II (*continued*)

a) Homopolymers

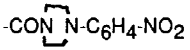
Nr.	n a b c	R	Transition temperatures (°C)
10	3 3 1 1	$-C_6H_4-Cl$	C 164 I
11	4 3 1 1	$-C_6H_4-Cl$	G 25 S_B 75 S_A 134 I
12	5 3 0 1	$-C_6H_4-Cl$	C 75 I
13	5 3 1 1	$-C_6H_4-Cl$	G 25 S_B 80 S_A 123 I
14	5 4 0 1	$-C_6H_4-Cl$	G 50 S_E 94 S_A 115 I
15	5 5 0 1	$-C_6H_4-Cl$	G 10 S_E 67 S_A 99 I
16	5 6 0 1	$-C_6H_4-Cl$	G 2 S_E 33 S_A 120 I
17	6 3 1 1	$-C_6H_4-Cl$	G 27 S_B 82 S_A 130 I
18	7 3 1 1	$-C_6H_4-Cl$	G 29 S_B 68 S_A 123 I
19	3 3 1 1	$-C_6H_4-OMe$	C 175 I
20	4 3 1 1	$-C_6H_4-OMe$	G 26 N 107 I
21	5 3 0 1	$-C_6H_4-OMe$	G 18 N 35 I
22	5 3 1 1	$-C_6H_4-OMe$	G 21 N 82 I
23	5 4 0 1	$-C_6H_4-OMe$	G 10 N 50 I
24	5 5 0 1	$-C_6H_4-OMe$	G 0 N 44 I
25	5 6 0 1	$-C_6H_4-OMe$	G -7 N 65 I
26	6 3 1 1	$-C_6H_4-OMe$	G 22 N 84 I
27	7 3 1 1	$-C_6H_4-OMe$	G 23 N 83 I
28	4 3 1 1	$-C_6H_4-O(CH_2)_3H$	G 32 N 112 I
29	6 3 1 1	$-C_6H_4-O(CH_2)_3H$	G 30 N 94 I
30	7 3 1 1	$-C_6H_4-O(CH_2)_3H$	G 27 N 89 I
31	4 3^* 0 1	$-C_6H_4-C_6H_4-CN$	G 52 S_X 113 S_A 221 I
32	4 3 1 1	$-C_6H_4-C_6H_4-CN$	G 59 S_A >300 I
33	410 0 0	 $-CON\ N-C_6H_4-NO_2$	G 27 S_A 98 I
34	3 3^* 0 1	-Chol	G 63 S_A 149 I
35	4 3^* 0 1	-Chol	G 67 S_A 164 I
36	4 3 1 1	-Chol	G 70 S_B 88 S_A 240 N^* 271 I
37	5 3^* 0 1	-Chol	G 80 S_A 187 I
38	5 3 0 1	-Chol	G 82 S_A 246 I
39	5 4 0 1	-Chol	G 65 S_A 240 I
40	5 5 0 1	-Chol	G 51 S_A 255 I
41	5 6 0 1	-Chol	G 40 S_A 248 I

TABLE II (*continued*)

b) Copolymers

Nr.	n a b c x	R	λ_R (nm)	Transition temperature (°C)
42	4 3 1 0 .25 0 0 0	$-C_6H_4-C_6H_4-$ -Me		C 81 I
43	4 4 0 1 .25 0 0 0	$-C_6H_4-C_6H_4-CN$ -Me		C 108 S_A 152 I
44	4 6 0 1 .25 0 0 0	$-C_6H_4-C_6H_4-CN$ -Me		C 82 S_A 167 I
45	4 6 0 1 .25 0 0 0	$-C_6H_4-C_6H_4-(CH_2)_4H$ -Me		C 28 I
46	4 3 1 1 .25 0 0 0	$-C_6H_4-C_6H_4-(CH_2)_5H$ -Me		C 98 S_B 101 I
47	4 6 1 1 .25 0 0 0	$-C_6H_4-C_6H_4-(CH_2)_5H$ -Me		C 76 S_B 123 I
48	4 6 1 1 .25 0 0 0	$-C_6H_4-C_6H_4-(CH_2)_2H$ -Me		C 87 S_C 115 I
49	4 6 0 1 .25 0 0 0	$-C_6H_4-C_6H_4-(CH_2)_5H$ -Me		C 45 I
50	4 3 1 0 .25 0 0 0	$-C_6H_4-CO-N\ N-C_6H_4-NO_2$ -Me		C 89 (G 11 S_A 54) I
51	410 0 0 .25 0 0 0	$-CO-N\ N-C_6H_4-NO_2$ -Me		G 0 S_A 57 I
52	4 3 0 1 .25 0 0 0	-Chol -Me		C 114 S_A 121 I
53	4 3 1 1 .25 0 0 0	-Chol -Me		G 58 S_B 81 S_A 115 I
54	4 4 1 1 .25 0 0 0	-Chol -Me		C 94 S_A 144 I
55	4 6 1 1 .25 0 0 0	-Chol -Me		C 67 S_A 156 I
56	4 3 1 1 .30 3 1 1	-Chol $-C_6H_4-CN$		G 51 S_A 165 N^* 218 I

TABLE II (*continued*)

57	5 3 0 1 .15 4 0 1	-Chol $-C_6H_4$-OMe	640	G 15 N^* 84 I
58	5 3 0 1 .35 4 0 1	-Chol $-C_6H_4$-OMe	460	G 26 N^* 141 I
59	5 3 0 1 .50 4 0 1	-Chol $-C_6H_4$-OMe	422	G 38 N^* 176 I
60	5 3 0 1 .60 4 0 1	-Chol $-C_6H_4$-OMe	436	G 47 N^* 196 I
61	3 3^*0 1 .33 3^*0 1	-Chol $-C_6H_4-C_6H_5$		G 41 S_A 100 I
62	3 3^*0 1 .67 3^*0 1	-Chol $-C_6H_4-C_6H_5$		G 47 S_A 115 I
63	4 3 1 1 .20 3 1 1	-Chol $-C_6H_4-C_6H_5$	1130	G 55 N^* 186 I
64	4 3 1 1 .30 3 1 1	-Chol $-C_6H_4-C_6H_5$	865	G 55 N^* 196 I
65	4 3 1 1 .35 3 1 1	-Chol $-C_6H_4-C_6H_5$	755	G 50 N^* 197 I
66	4 3 1 1 .40 3 1 1	-Chol $-C_6H_4-C_6H_5$	680	G 56 N^* 220 I
67	4 3 1 1 .50 3 1 1	-Chol $-C_6H_4-C_6H_5$	590	G 55 N^* 214 I
68	5 3 1 1 .20 3 1 1	-Chol $-C_6H_4-C_6H_5$	960	-
69	5 3 1 1 .30 3 1 1	-Chol $-C_6H_4-C_6H_5$	690	-
70	5 3 1 1 .35 3 1 1	-Chol $-C_6H_4-C_6H_5$	630	G 52 N^* 199 I
71	5 3 1 1 .40 3 1 1	-Chol $-C_6H_4-C_6H_5$	570	-

TABLE II (*continued*)

72	5 3 1 1 .50 3 1 1	-Chol $-C_6H_4-C_6H_5$	520	G 50 N^* 216 I
73	5 4 0 1 .50 4 0 1	-Chol $-C_6H_4-C_6H_5$		G 44 S_A 184 N^* 207 I
74	5 6 1 1 .33 6 1 1	-Chol $-C_6H_4-C_6H_5$		G 35 S_A 163 N^* 199 I
75	5 6 1 1 .50 6 1 1	-Chol $-C_6H_4-C_6H_5$		G 41 S_A 194 N^* 216 I
76	6 3 1 1 .20 3 1 1	-Chol $-C_6H_4-C_6H_5$	880	G 48 N^* 180 I
77	6 3 1 1 .30 3 1 1	-Chol $-C_6H_4-C_6H_5$	640	G 52 N^* 194 I
78	6 3 1 1 .35 3 1 1	-Chol $-C_6H_4-C_6H_5$	560	G 55 N^* 200 I
79	6 3 1 1 .40 3 1 1	-Chol $-C_6H_4-C_6H_5$	520	G 60 N^* 226 I
80	6 3 1 1 .50 3 1 1	-Chol $-C_6H_4-C_6H_5$	480	G 58 N^* 217 I
81	410 0 0 .50 10 0 0	-COO-Chol $-COO-C_6H_4-C_6H_5$		G 17 S_A 102 I

3*: $-(CH_2)_2-Si(CH_3)_2-$ instead of $-(CH_2)_3-$.

side groups (Figure 21) like copolymers of higher degree of polymerization or mixtures of monomeric liquid crystals.

It is also possible to obtain copolymeric CLCS with only one mesogenic group in the molecule (**42–55**). In this case the ratio of the monomer units in all molecules is the same. These materials can polymerize. By polymerization of copolymers with two siloxane rings e.g. compound **42** highly ordered networks could be obtained (Figure 22a, b).

Table II shows the phase behaviour of several CLCS.

3.4.4 Influences on the wavelength of reflection of cholesterics. The wavelength of reflection of cholesteric CLCS copolymers depends not only on the chemical

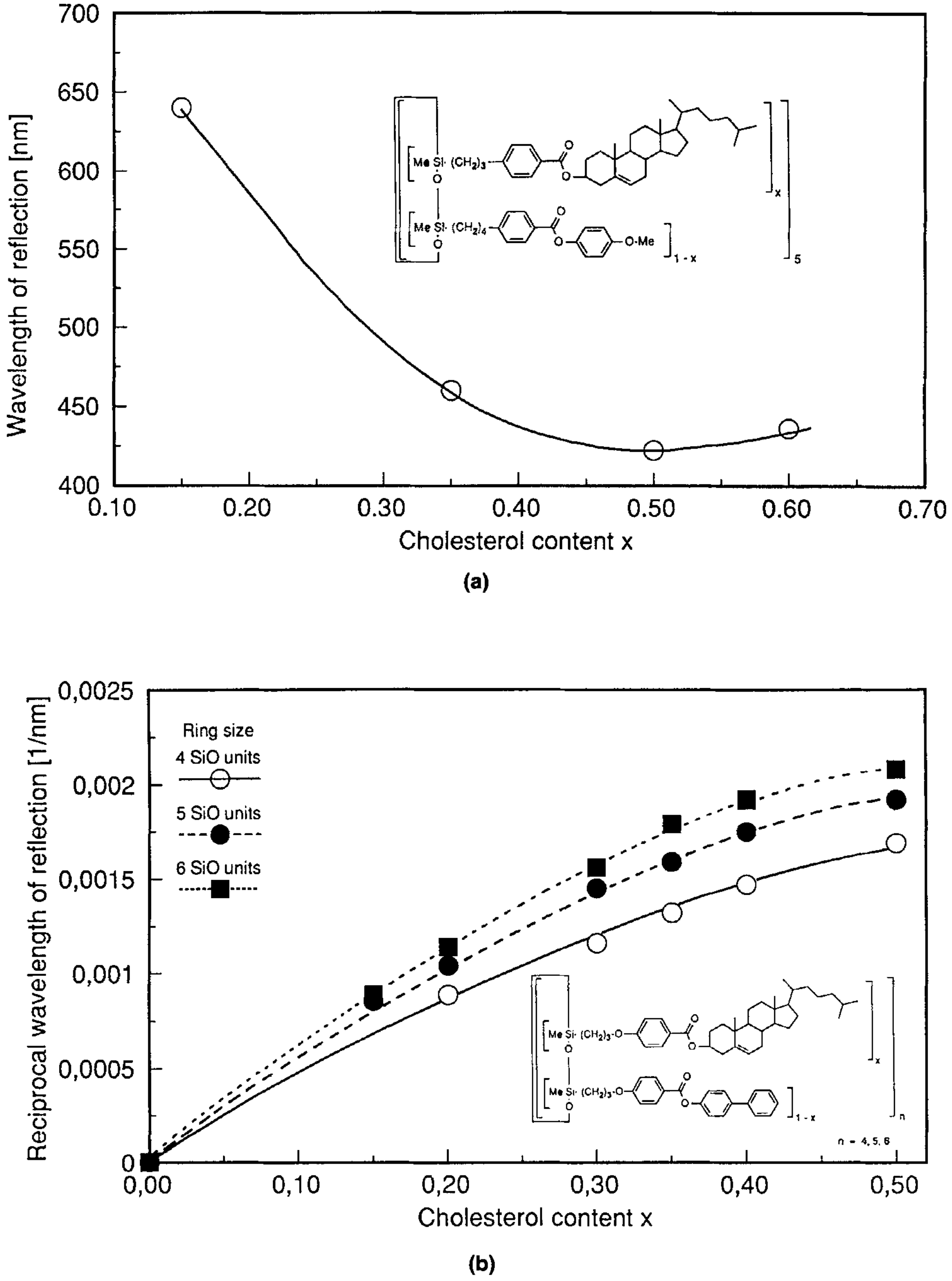


FIGURE 23 a) Dependence of wavelength of reflection on cholesterol content. b) Influence of the ring size on the helical twisting power. The larger the number of Si atoms in the siloxane ring the higher the helical twisting power of cholesterol group.

TABLE III

X-Ray measurements

a) Homopolymers

Nr.	n a b c	R	d_c	d_{s1}	d_{s2}	d_w
11	4 3 1 1	$-C_6H_4-Cl$	17.4	18.9	-	4.5
13	5 3 1 1	$-C_6H_4-Cl$	17.4	19.5	-	4.5
17	6 3 1 1	$-C_6H_4-Cl$	17.4	19.1	-	4.5
18	7 3 1 1	$-C_6H_4-Cl$	17.4	18.6	-	4.4
31	4 3^* 0 1	$-C_6H_4-C_6H_4-CN$	20.8	26.0	13.0	4.4
32	4 3 1 1	$-C_6H_4-C_6H_4-CN$	22.6	24.0	-	4.4
33	410 0 0	$-CON\ N-C_6H_4-NO_2$	23.3	37.6	19.0	4.6
34	3 3^* 0 1	-Chol	28.4	28.9	-	5.4
35	4 3^* 0 1	-Chol	28.4	27.7	-	5.4
36	4 3 1 1	-Chol	30.1	28.3	-	5.3
37	5 3^* 0 1	-Chol	28.4	27.7	-	5.4
38	5 3 0 1	-Chol	28.5	27.7	-	5.4
39	5 4 0 1	-Chol	29.9	29.0	-	5.2
40	5 5 0 1	-Chol	31.1	30.0	-	5.3
41	5 6 0 1	-Chol	32.4	31.2	-	5.2

b) Copolymers

with one mesogenic group

Nr.	n a b c x	R	d_c	d_{s1}	d_{s2}	d_w
50	4 3 1 0 .25 0 0 0	$-C_6H_4-CO-N\ N-C_6H_4-NO_2$ -Me	20.2	34.7	-	4.2
51	410 0 0 .25 0 0 0	$-CO-N\ N-C_6H_4-NO_2$ -Me	23.3	41.4	21.1	4.2

TABLE III (*continued*)

54	4 4 1 1 .25 0 0 0	-Chol -Me	31.4	29.1	14.4	5.2
55	4 6 1 1 .25 0 0 0	-Chol -Me	33.7	33.5	17.8	5.2
	with two mesogenic groups					
56	4 3 1 1 .30 3 1 1	-Chol -C_6H_4-CN	30.12 18.32	27.2	-	5.1
61	3 3*0 1 .33 3*0 1	-Chol C_6H_4-C_6H_5	28.36 19.18	26.8	13.6	5.0
62	3 3*0 1 .67 3*0 1	-Chol -C_6H_4-C_6H_5	28.4 19.2	28.0	14.2	5.3
73	5 4 0 1 .50 4 0 1	-Chol -C_6H_4-C_6H_5	29.8 20.7	25.8	-	4.9
74	5 6 1 1 .33 6 1 1	-Chol -C_6H_4-C_6H_5	32.7 24.3	27.0	-	4.6
75	5 6 1 1 .50 6 1 1	-Chol -C_6H_4-C_6H_5	32.7 24.3	27.4	-	4.8
81	410 0 0 .50 10 0 0	-COO-Chol -COO-C_6H_4-C_6H_5	32.4 23.6	30.3	-	4.8

d_c: calculated length of the mesogenic group including the Si atom of the siloxane ring,
d_{s1}: small angle reflex 001,
d_{s2}: small angle reflex 002,
d_w: wide angle reflex, in Å.

composition (Figure 23a). The ring size of the siloxane backbone also is important. The helical twisting power of the chiral component is the weaker the smaller the ring size (Figure 23b).

3.5 X-Ray Measurements (Table III)

3.5.1 Influence of the ring size and the spacer length. The influence of the ring size onto the distances of S_A or S_B layers is relatively weak (Figure 24). By variation

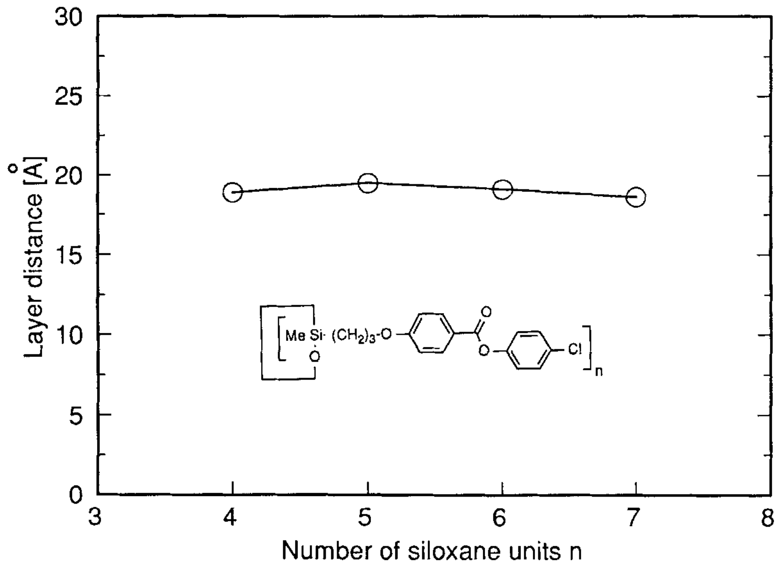


FIGURE 24 Influence of ring size on layer distance. The thicknesses of S_A layers are nearly independent on the ring size of CLCS.

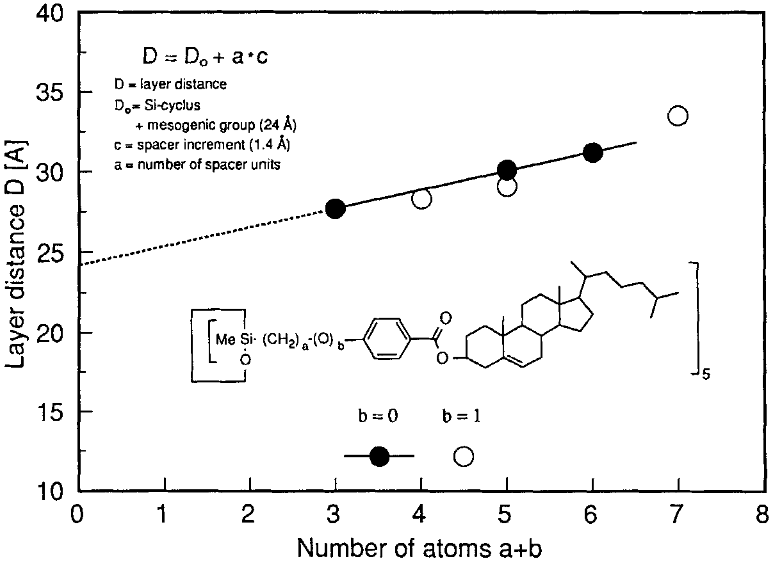
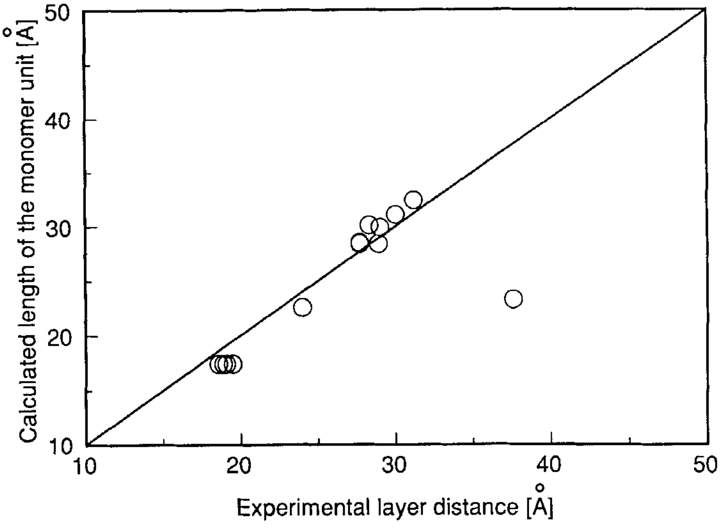


FIGURE 25 Influence of spacer length on layer distance. The distances of S_A layers of CLCS depend on the spacer length. The extrapolation of $n = 0$ yields the length of the cholesteryl benzoate molecule.



Experimental and calculated layer distances

FIGURE 26 Experimental and calculated layer distances of CLCS. The experimental distances of smectic A and B layers fit the calculated lengths of the mesogenic groups. A compound with a high polarizable mesogenic group deviates from this system. In this case a partial interdigitating is assumed.

of the spacer length the contribution of a CH_2-group to the layer distance was determined to be 1.4 Å and is in good agreement with the theoretical value, also is the extrapolated length of the monomer unit (exp.: 24 Å, calc. 23.5 Å, Figure 25).

3.5.2 Correlation between the lengths of the mesogenic groups and the layer distances of smectic A and B phases. Many examples exhibit a good correlation between layer distances of smectic A and B phases of CLCS and the calculated lengths of the monomer units (Figure 26). This is also observed in the linear series.[28] For copolymers the 1.05 fold length of the mean value of the mesogenic groups is a good approximation. Materials with very high polarizable mesogens deviate from this scheme (**33**).

These molecules can dimerize so they show a tendency of paired structures like low molecular weight liquid crystals.[29,30] To be sure that the layer distances used are not of second order the small angle area was screened by a small angle Kratky camera (Figure 27). The peculiarities of materials with mesogens of high polarizability are also indicated by reflexes up to the 4. order (Figure 28).

Surprisingly the materials with only one mesogenic group are in accordance with this scheme (**50–55**). But more detailed investigations have to be done. Paired and interdigitating models were proposed for linear liquid crystalline side chain siloxanes earlier.[28–31] The X-ray measurements of smectic CLCS with mesogens of low or high polarity or polarizability are in accordance with bundle structures arranged in paired or interdigitating layers (Figure 29).

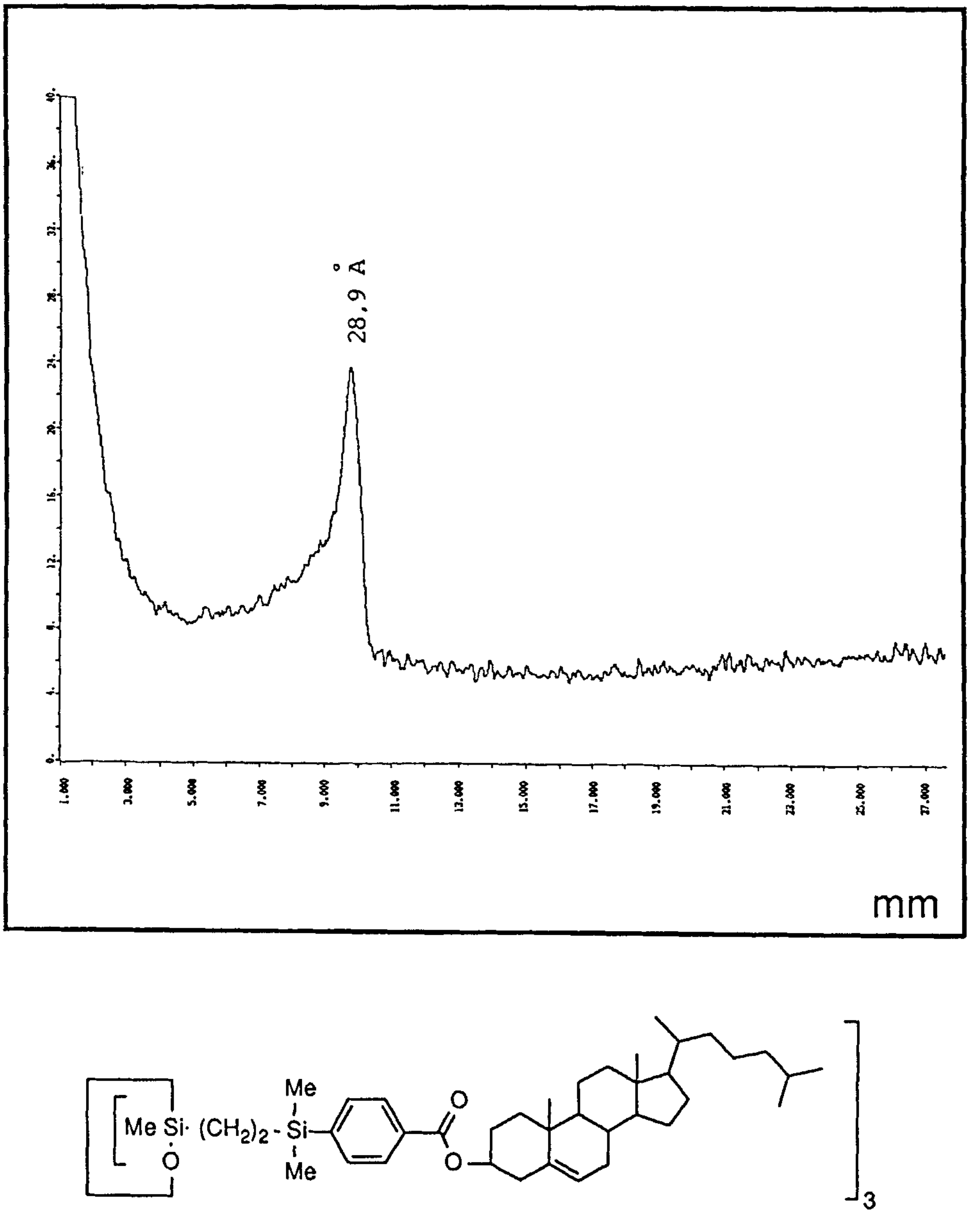
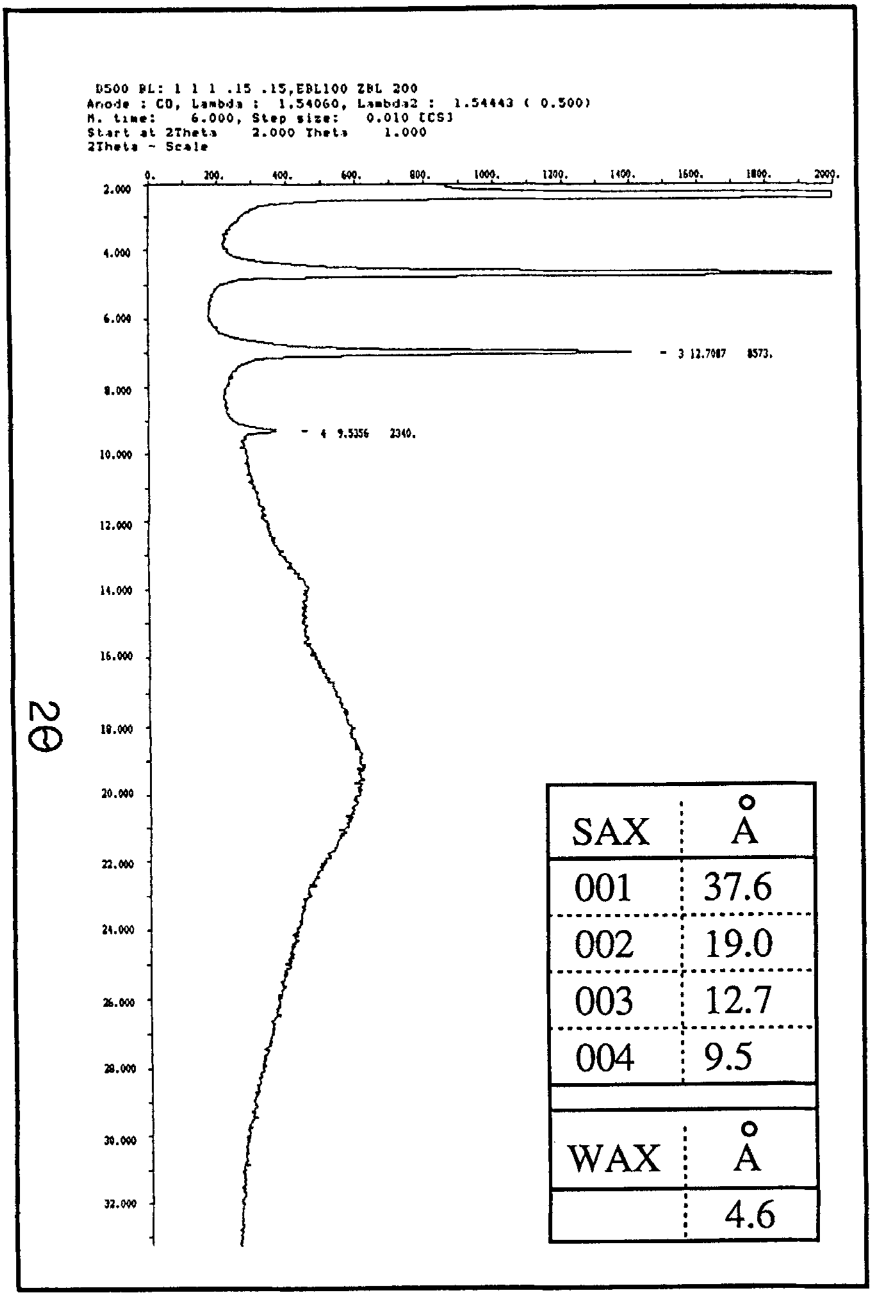


FIGURE 27 SAX diffraction pattern of **34**.



SAX	Å
001	37.6
002	19.0
003	12.7
004	9.5

WAX	Å
	4.6

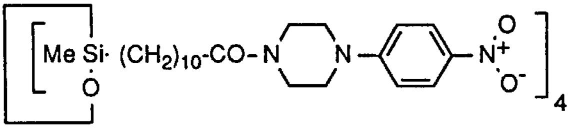


FIGURE 28 X-Ray diffraction pattern of **33**.

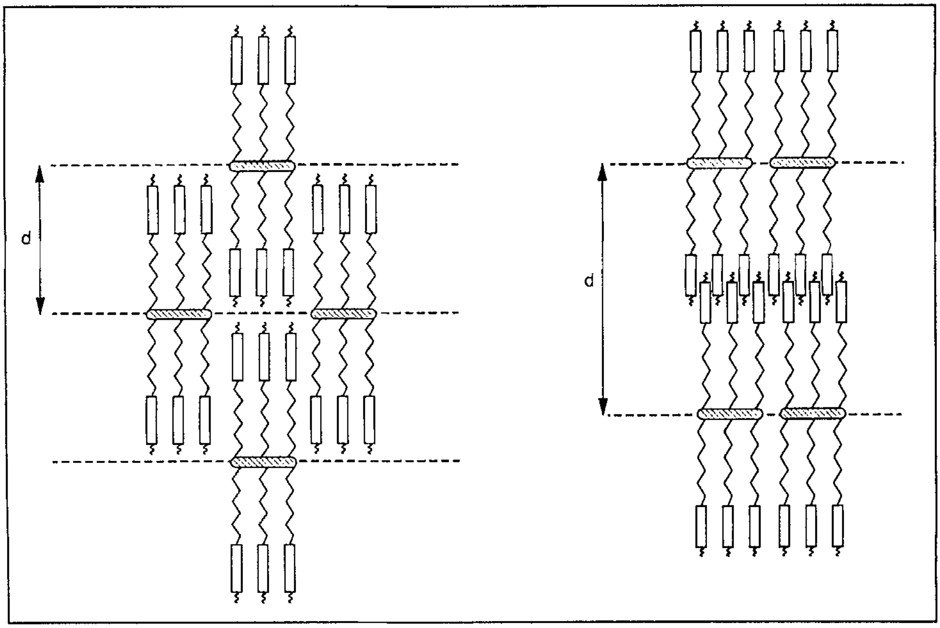


FIGURE 29 Possible smectic structures of CLC-siloxanes.

4. SUMMARY

Cyclic liquid crystalline siloxanes (CLCS) have properties like other calamitic liquid crystals of low or high molecular weight. They exhibit smectic, nematic, or cholesteric phases. Homeotropic oriented nematic and smectic A and B phases of CLCS are optical uniaxial positive. We assume that CLCS have the shape of bundles arranged in paired or interdigitating structures.

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