Thermal Behaviour and Mesophase Structure of Cyclic Oligosiloxanes With Chiral Mesogenic Groups

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THERMAL BEHAVIOUR AND MESOPHASE STRUCTURE OF CYCLIC OLIGOSILOXANES WITH CHIRAL MESOGENIC GROUPS

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Chiral, smectogenic pendant groups have been covalently attached to cyclic oligosiloxanes by hydrosilylation. Differential scanning calorimetry, optical polarising microscopy, and X-ray diffraction measurements reveal liquid crystalline properties for all synthesized monomers and oligomers. The monomers, which differ by the nature of the rigid mesogenic core or end groups, showed enantiotropic smectic A phases. Almost all of cyclic oligosiloxanes present enantiotropic chiral smectic C phases. The mesomorphic range of these oligomers is greatly enhanced relative to the type of monomers and the ring size as well.

*Keywords*: cyclic oligosiloxanes; liquid crystals; smectic mesophase

INTRODUCTION

The design and synthesis of chiral thermotropic side-chain liquid crystalline polymers (SCLCPs) are currently the focus of intense research [1,2]. The ability of these polymers to generate chiral nematic and chiral smectic

supramolecular assembles endowed with a macroscopic twist can result in the availability of new materials with promising optical and electro-optical properties for various potential high-tech applications. The advantage of liquid crystalline polysiloxanes, compared to other SCLCPs, lies in their high backbone flexibility, due to the presence of siloxane units, which results in relatively low glass and mesophase transitions. Therefore one limitation of SCLC polymers, particularly with respect to their use for optical data storage, is their high viscosity. Within the group of SCLC polysiloxanes, a significant interest concentrates recently on small ring systems with mesogenic units as substituents at silicon atoms. The development of cyclic oligosiloxanes with mesogenic groups has shown that these materials exhibit properties intermediate to low molecular weight liquid crystals and polymeric ones. This class of materials combines the low melt viscosity of conventional low molar weight LC with the glass-forming ability (above ambient temperature) of conventional polymer structures. Moreover, the absence of any polydispersity in some oligomers, which is by contrast an inherent property in polymers, facilitates the reproducibility of liquid crystal properties [3–7].

Until now the esters of cinnamic acid were not attached as pendant groups to cyclic oligosiloxanes. In order to obtain new materials with ferroelectric properties and also to study the influence of a cinnamate function on the existence and stability of SmC* phase, we have synthesised a series of oligocyclosiloxanes with a mesogenic unit of general formula **1**:

$$-(CH_2)_nO-\!\!\!\!\bigcirc\!\!\!\!-CH\!=\!CH-COO-\!\!\!\!\bigcirc\!\!\!\!-COOCH_2\overset{*}{C}HCH_2CH_3$$
$$CH_3$$
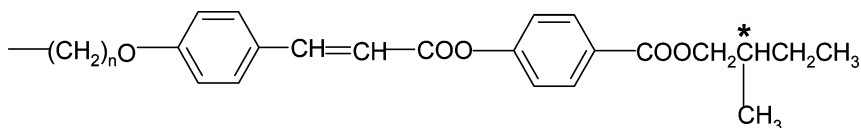
They were compared with biphenyl and benzoyloxyphenyl mesogenic rigid cores; (*S*)-2-methylbutanol, (2*S*)-2-chloro-4-methylpentanoic acid or (2*S*,3*S*)-2-chloro-3-methylpentanoic acid were used as chiral substituents.

A schematic representation of all of the synthesized compounds is shown in Figure 1.

EXPERIMENTAL

General

All chemicals were of commercial grade quality and used without further purification. Solvents were distilled by conventional methods prior to use. The hydrosilylation catalyst -platinum tetramethyldivinyl disiloxane complex in xylene (11% wt) was obtained from GE Silicon.

x=4,5,6; n=5,8,11; Y=none, -COO-, -CH=CHCOO-

R= —CH=CHCOOCH₂C̲HCH₂CH₃ ; —CH=CHCOO—⟨◯⟩—COOCH₂C̲HCH₂CH₃ ; —COOCH₂C̲HCH₂CH₃ ; —OOCCHR₁
            CH₃   CH₃   CH₃   Cl

R₁= —CH₂CH(CH₃)₂ ; —C̲HCH₂CH₂
                     CH₃
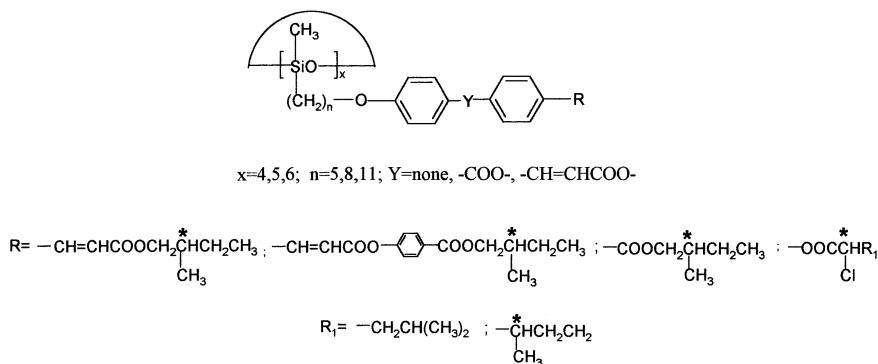
FIGURE 1 General structure of cyclic oligosiloxanes with pendant groups.

¹H NMR were collected on a VARIAN INOVA (500 MHz) spectrometer, using deuterated chloroform as a solvent and tetramethylsilane as the internal standard. FTIR spectra were obtained using a Perkin-Elmer SPEC-TRUM 2000 spectrometer. Monomer and oligomer samples were prepared as either potassium bromide discs, or if liquid, were run on single crystal sodium chloride discs.

Differential Scanning Calorimetry (DSC) thermograms were obtained using a Perkin ELMER DSC-7, with A TAC 7/PC interface and a controlled cooling accessory. The transition temperatures were taken from DSC traces of samples annealed by cooling from the isotropic melt as corresponding to the maxima and the onset points of the enthalpic peaks for polymers and low molecular weight samples, respectively, at a heating rate of 10℃/min⁻¹. Optical microscopy was performed using a Biolar polarising microscope, fitted with a Mettler FP82HT heating stage and a Mettler FP-90 processor. Samples were prepared as thin films between glass slide and a glass cover slip.

X-ray diffraction measurements have been performed using a Philips X'Pert diffractometer as well as a Guinier symmetrical focusing trans-mission photographic camera. In the case of diffractometer copper radiation filtered by nickel absorption filter was applied, while Guinier camera worked with cobalt radiation. Diffractometer smectic phase measurements were carried out using the reflecting method from flat sample aligned by glass substrate. The chosen temperature was maintained within ±0.1℃.

Synthesis

The alkene mesogenic side chain precursors used in the hydrosilylation reactions were prepared by standard methods. (*S*)-2-methylbutyl,

(*S*)-1-chloro-3-methylbutanocarbonyl and (1*S*, 2*S*)1-chloro-2-methylbutano-carbonyl were used as chiral substituents.

The *trans*-alkenyloxy cinnamic acids were obtained starting from the 4-hydroxybenzaldehyde in a series of following reactions: etherification of the 4-hydroxybenzaldehyde with an appropriate bromoalkene or tosy-late and subsequent Knoevenagel condensation between the aldehyde and the malonic acid in the presence of piperidine and pyridine. The (*S*)-2-methylbutyl 4-hydroxybenzoate was obtained in the direct esterifi-cation of 4-hydroxybenzoic acid with (*S*)-2-methylbutanol in the presence of p-toluenesulfonic acid.

The final compounds **M1–M3** were obtained by esterification of the cinnamic acid and (*S*)-2-methylbutyl 4-hydroxybenzoate in the presence of DCC and DMAP (Scheme 1).

They were purified by chromatography on silica gel with chloroform as eluent. Monomers M5 and M6 were also obtained by similar procedure.
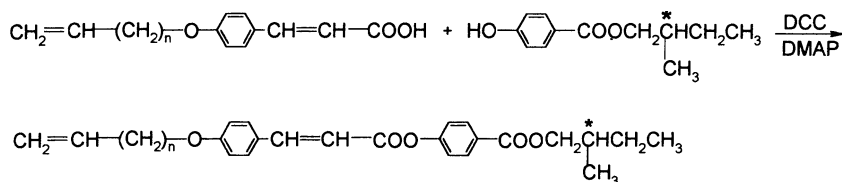
The mesogene M4 was prepared starting from the 4-hydroxybenzoic acid methyl ester in a series of following reactions: alkylation of 4-hydroxy-benzoic acid methyl ester with undec-10-enyl tosylate (KOH, ethanol), subsequent hydrolysis of methyl ester and final esterification of 4-(undec-10-enyloxy)benzoic acid and (*S*)-2-methylbutyl 4-hydroxybenzo-ate in the presence of DCC and DMAP.

The synthesis of 4-(4′-undec-10-enyloxy)biphenyl esters of (2*S*)-2-chloro-4-methylpentanoic (M7) or (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (M8) is outlined at the Scheme 2:
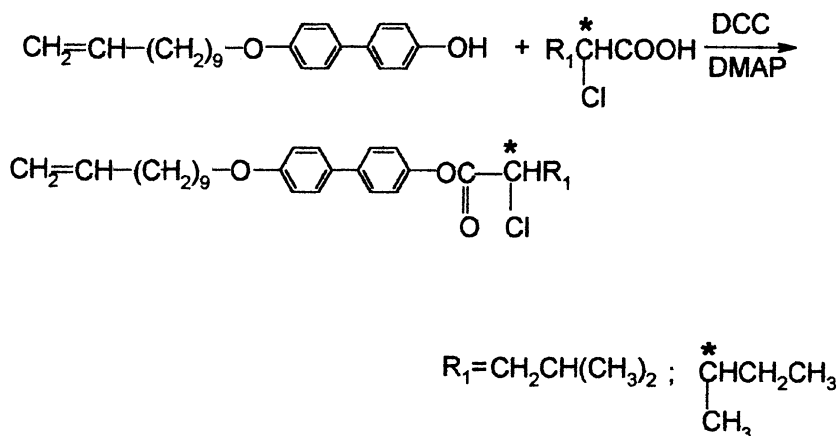
4-hydroxy-(4′-undec-10-enyloxy)biphenyl was prepared following a method reported in the literature [8].

α-Chloroacids were prepared from the corresponding α-aminoacids (L-leucine and L-isoleucine) according to the procedure of Schacht [9] (Scheme 3).

We have found only an inconsiderable degree of racemisation [α] = −2,8° for (2*S*,3*S*)-2-chloro-3-methylpentanoic acid ([α]$_{lit.}$ −2,9° [10]). The structures of final products (new compounds except M4) were confirmed by means of FTIR, ^{1}H NMR. Spectral data of M1–M3 (Table 1)
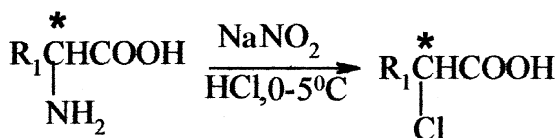

SCHEME 1

$CH_2{=}CH{-}(CH_2)_9{-}O{-}$⬡⬡$-OH$ + $R_1\overset{*}{C}HCOOH$ $\xrightarrow[\text{DMAP}]{\text{DCC}}$
                                                                  $|$
                                                                  Cl

$CH_2{=}CH{-}(CH_2)_9{-}O{-}$⬡⬡$-O\overset{}{C}{-}\overset{*}{C}HR_1$
                                        $\underset{O}{\|}\ \ \underset{Cl}{|}$

$R_1{=}CH_2CH(CH_3)_2$; $\overset{*}{C}HCH_2CH_3$
                        $|$
                        CH_3

SCHEME 2

and M7 are given as an example; values of other homologous compounds were similar.

Monomer 7: ^{1}H NMR (ppm CDCl$_3$): δ 1.01(d, 3H, CH(C**H$_3$**)), 1.04(d, 3H, CH(C**H$_3$**)), 1.31–2.02 (m, 22H), 3.99 (t, 2H OC**H$_2$**), 4,55 (t, 1H, C**H**Cl), 4.90–5.05 (m, 2H, C**H$_2$** $=$ C), 5.72–5.92 (m, 1H, CH$_2$ $=$ C**H**), 6.94–7.53 (m, 8H, Ar-**H**).

The thermal properties of monomers are summarized in Table 2.

General procedure for hydrosilylation of cyclic oligosiloxanes with olefin terminated mesogens:

In a typical hydrosilylation reaction (Fig. 2), 0.52 g (1.03 mmol) (*E*)-3-[4-undec-10-enyloxy)phenyl]-cinnamic acid 4[(*S*)-2-methylbutoxy)carbonyl]phenyl ester was dissolved under nitrogen in dry (sodium mirror) toluene and then 56 mg (0.93 mmol of SiH–units) of 2,4,6,8-tetramethyl-cyclotetrasiloxane was added under a nitrogen into a Schlenk tube containing the solution. After addition of a catalyst (-4 ml of 11% PTDD solution in xylene 2×10^{-4} mol Pt/mol^{-1} SiH) – the reaction was carried out for 24 h, with magnetic stirring, at room temperature. During that time

$R_1\overset{*}{C}HCOOH$ $\xrightarrow[\text{HCl,0-5}^0\text{C}]{\text{NaNO}_2}$ $R_1\overset{*}{C}HCOOH$
        $|$ $|$
        NH_2 Cl

SCHEME 3

TABLE 1 The ^{1}H NMR Chemical Shifts (δ ppm) of the Mesogens M1-M3

Proton numbers	Mesogens		
	M1 (n = 2)	M2 (n = 5)	M3 (n = 8)
1	5.07 (m)	5.02 (m)	4.96 (m)
2	5.85 (m)	5.82 (m)	5.82 (m)
3	1.91–2.25 (m, 4H)	1.42–1.62 (m, 10H)	1.29–1.54 (m, 16H)
4	4.02 (t)	4.01 (t)	4.05 (t)
5	6.93 (d)	6.92 (d)	6.97 (d)
6	7.53 (d)	7.53 (d)	7.54 (d)
7	7.84 (d)	7.84 (d)	7.39 (d)
8	6.48 (d)	6.48 (d)	6.58 (d)
9	7.25 (d)	7.25 (d)	7.25 (d)
10	8.10 (d)	8.10 (d)	8.10 (d)
11	4.22 (m)	4.21 (m)	4.21 (m)
12	1.87 (m)	2.10 (m)	2.05 (m)
13	1.02 (d)	1.02 (d)	1.02 (d)
14	1.29 (m)	1.28 (m)	1.28 (m)
15	0.97 (t)	0.97 (t)	0.97 (t)

the colourless solution turned pale brown due to the formation of colloidal platinum. The temperature was then raised and process was continued for another 48 h at 55–60℃. FTIR analysis of the solution (NaCl cell windows) showed the absence of a SiH band at $2165\,\mathrm{cm}^{-1}$, indicating the hydrosilylation was complete. The SCLC cyclic tetramer was separated, purified by several reprecipitations from toluene solution into methanol and filtered through a disposable syringe filter (PTFE membrane 0,45 μm) to remove any particulates. The solvent was carefully removed by rotary evaporation and the tetramer dried in vacuum.

The structures of oligomers were confirmed by FTIR and ^{1}H NMR. Spectral data of D4M3 are given as an example.

^{1}H NMR (ppm CDCl$_3$): δ 0.11(s, 12H, SiC**H**$_3$), 0.59(m, 8H, SiC**H**$_2$), 0.95(m, 12H C**H**$_3$), 1.28–1.82 (m, 104H, C**H**$_2$ and C**H**$_3$), 1.87 (m, 4H, C**H**), 4.05 (m, 8H, OC**H**$_2$), 6.48 (d, 4H, =C**H**COO), 6.93 (d, 8H Ar-**H**), 7.25 (d, 8H, Ar-**H**), 7.53 (d, 8H, Ar-**H**), 7.84 (d, 4H, Ar-C**H**=), 8.10 (d, 8H, Ar-**H**).

FTIR (cm^{-1}, KBr)γ_{max} 3000–2840, 1726, 1633, 1605, 1560, 1280, 760, absence of 2165 (SiH).

**TABLE 2** The Properties of Mesogenes with Chiral end Groups M1–M8

$$CH_2=CH\text{-}(CH_2)_n\text{-}O\text{-}\text{-}Y\text{-}\text{-}R$$
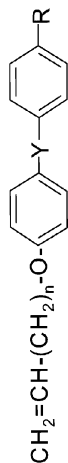
No	n	Y	R	Phase transition temperature*/°C	d(Å)	l*(Å)	d/l
M1	3	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	Cr 63.5 SmA 82.5 I	29.3	23.1	1.26
M2	6	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	Cr 53.3 SmA 82.5 I	30.5	26.0	1.17
M3	9	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	Cr 42.2 SmA 89.3 I	31.8	30.5	1.04
M4	9	COO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	Cr 43.6 SmA 50.3 I	31.3	29.0	1.07
M5	9	COO	CH=CHCOOC$_6$H$_4$COOCH$_2$CH(CH$_3$)C$_2$H$_5$	Cr 50.4 SmC * 184 I	40.2	41.7	0.96
M6	9	COO	CH=CHCOOCH$_2$CH(CH$_3$)C$_2$H$_5$	Cr1 22 Cr2 39 SmA 82.5 I	39.1	31.0	1.26
M7	9	–	OOCCH(Cl)CH$_2$CH(CH$_3$)$_2$	Cr 65 I	–	–	–
M8	9	–	OOCCH(Cl)CHCH$_3$C$_2$H$_5$	Cr 50 SmA 58.4 I	–	–	–

From DSC second heating cycle, (10°C/min heating rate); Cr-crystalline phase, SmA-smectic A phase, SmC-chiralsmectic C phase, I-isotropic phase.
**l: calculated length of monomers in its fully extended conformation (semiempirical AM1,Hyper-Chem).
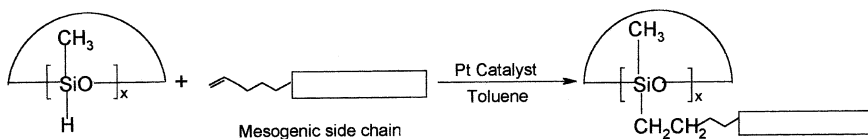
FIGURE 2 The hydrosilylation reaction.

The other oligomers were prepared according to the procedure described above. The thermal properties of oligomers are summarized in Table 3.

RESULTS AND DISCUSSION

As can be seen from the data listed in Table 2, monomers M1–M3 with cinnamic moiety in mesogenic core exhibit smectic A phases, within a differentiate temperature range. The thermal stabilities of the smectic A phases were increased with increasing the length of spacer from 5 (M1) to 11 (M3) carbon atoms.

Moreover, from the transitions on heating for M3 and M4 (Table 2) we could clearly observe that the monomer M3 exhibited a wider smectic phase than the M4 compound. The difference between these monomers is the nature of the mesogenic core. The benzoiloxyphenyl core (M4) leads to narrow smectic phase only within 7 degrees , while cinnamic ester core leads to smectic phase observable within 47 degrees. These results suggest that monomer M3 posseses greater propensity to give rise to stable smectic mesophase than do the monomer M4, thus indicating that the replacement of benzoiloxyphenyl core by the cinnamoiloxy phenyl group strongly enhances the smectogenic character of the monomer. In addition, the monomer M5, which incorporates three phenyl rings in its structure exhibits, the widest range of the chiral smectic mesophase. The change of the position of the cinnamic substituent (M6) does not influence the transition temperatures greatly.

M7 and M8 monomers are alkenyloxybiphenyl esters of chiral 2-chloro-acids. Only one of them (2-chloro-3-methylpentanoic acid ester) exhibits LC properties with narrow range of SmA phase.

All oligomers showed liquid crystalline behaviours under observation with polarising microscope. In the case of cinnamic acid derivatives it was SmC* phase. The transition to the chiral smectic C phase was evident by the formation of pitch lines (arcs) in the broken focal conic texture, which breaks apart to form the broken focal conic characteristic for tilted smectics. The DSC analyses of the liquid crystalline properties of the all of the oligomers were measured by a glass transition or a melting transition

TABLE 3 The Properties of LC Cylic Oligosiloxanes
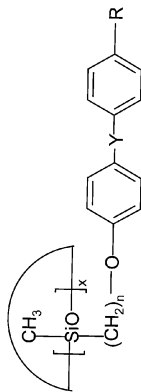
No	X	Y	R	n	Phase transition temperature*/°C	$d(\text{Å})$	$l(\text{Å})$	d/l
O4M1	4	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	5	g −9.8 SmC* 110 I	25.9	30.2	0.86
O4M2	4	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	8	g −0.9 SmC*134.6 I	29.1	33.3	0.87
O4M3	4	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g 2.6 SmC*133 I	34.1	37.4	0.91
O5M3	5	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g 1.5 SmC* 146 I	34.4	37.4	0.92
O6M1	6	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	5	g −17 SmC*58 I	29.3	30.2	0.97
O6M2	6	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	8	g −4.0 SmC*83.4 I	31.5	33.3	0.94
O6M3	6	CH=CHCOO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g 8.0 SmC*135 I	35.6	37.4	0.95
O4M4	4	COO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g −12 SmA111 I	32.0	32.7	0.98
O5M4	5	COO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g −13.8 SmA 115 I	32.3	32.7	0.99
O6M4	6	COO	COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g −18 SmA 112 I	32.8	32.7	1.00
O4M5	4	COO	CH=CHCOOC$_6$H$_4$COOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g −22 Sx 29.2 SmC*128 I	37.6	41.7	0.90
O4M6	4	COO	CH=CHCOOCH$_2$CH(CH$_3$)C$_2$H$_5$	11	g 40 SmC*54 SmA 161 I	34.3	37.5	0.91
O6M7	6	–	OOCCH(Cl)CH$_2$CH(CH$_3$)$_2$	11	Cr 76 SmC*92 SmA 117.6 I	32.0**	33.3	0.96
O6M8	6	–	OOCCH(Cl)CHCH$_3$C$_2$H$_5$	11	Cr 68.5 SmC*77.5 SmA 128.5 I	32.2**	33.3	0.96

From DSC second heating cycle, (10°C/min heating rate); Cr-crystalline phase, g-glassy, SmA-smectic A phase, SmC-chiral smectic phase, S$_x$-unidentified smectic phase, I-isotropic phase.

**In the SmA phase.

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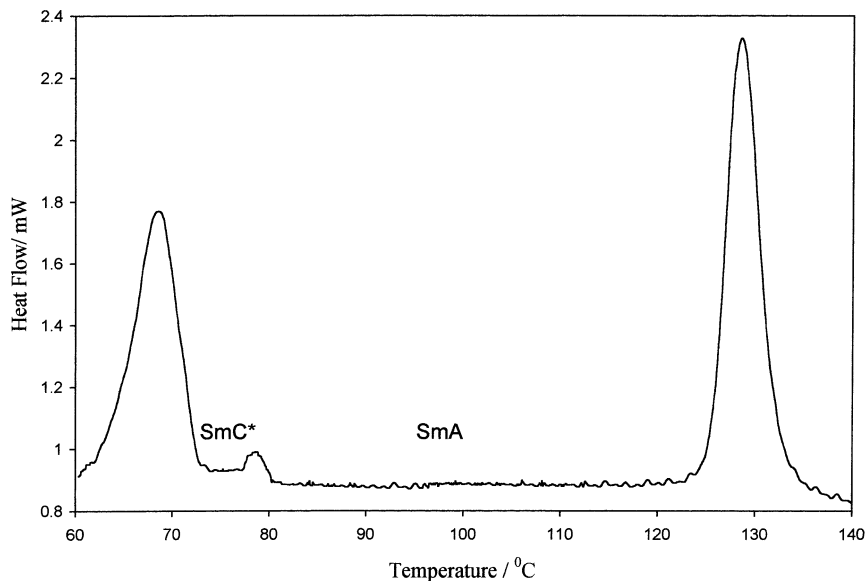
FIGURE 3 DSC thermogram of cyclic oligosiloxanes O6M8 ($10°C \, min^{-1}$): heating scan.

and one or two endotherm corresponding to an isotropic transition. The DSC thermograms of oligomer O6M8 are presented in Figure 3.

The characterization of the smectic mesophases was also carried out by temperature-controlled X-ray diffraction of powder samples. In general, the X-ray diagrams of the smectic phase exhibited two or three sharp reflections with Bragg molar spacing typical of layered structures in the low-angle region. The interlayer distance d exceeded a calculated molecular length l for almost all monomeric compounds (Table 2). This indicates the presence of the smectic A structure and the microscopic observations confirmed this assumption.

In the case of oligomers with phenyl cinnamate mesogenic core d/l ratios are between 0.85–0.95 and indicate the tilted smectic phase-SmC. The relatively higher d/l values for D_6 ring is probably connected with the mobility of the greater ring (Table 3). These values closely agree with earlier data on chiral polysiloxanes with a a three ring mesogenic rigid core and chiral 2-methylbutyl chain attached via sulfur atom [11]. Therefore, the mesogenic side groups are tilted to the layer normal in the smectic C mesophase [12] by an angle $\theta \approx 20$–$30°$. These X-ray data were supported by microscopic observations i.e. the formation of banded focal conic textures, characteristic for chiral smectic C phase.

In the homologous series O4M4–O6M6 (phenyl benzoate mesogenic core) the values of d were in close agreement with the lengths l of their respective side chains. In all the above samples, the smectic interlayer spacing d was practically constant from room temperature up to the isotropization point ($d=32.7$ Å at 20℃ and 32.8 at 80℃). This suggests the presence of an orthogonal disordered smectic, such as a smectic A_1 phase. These results demonstrate the superiority of phenyl cinnamate mesogenic unit to benzoiloxyphenyl in promoting LC properties.

The oligomers O6M7 and O6M8 exhibit two LC phases SmC* and SmA. Oligomer O6M8 exhibits a melting transition at 68.5℃ followed by a chiral smectic C to smectic A phase transition at 77.8℃ and the smectic A to isotropic phase transitionat 128.5℃.

Figure 4 shows the temperature dependent d-spacing of the both smectic layers obtained from powder samples of O6M8. At first, d-spacing increases with increasing temperature what is characteristic for smectic C phase, and than is almost stable (in the range about 50 degrees). Such behaviour indicates the existence of SmC phase at first and the SmA between 77.8. and 128.5℃. These results were confirmed by microscopic observations.

The influence of the ring size on the phase behaviour of cyclic oligosiloxanes was studied earlier [6,13,14]. Our own observations concerning siloxane rings up to six Si atoms indicate that the ring size should be considered in connection with the nature of mesogenic groups. Increasing or
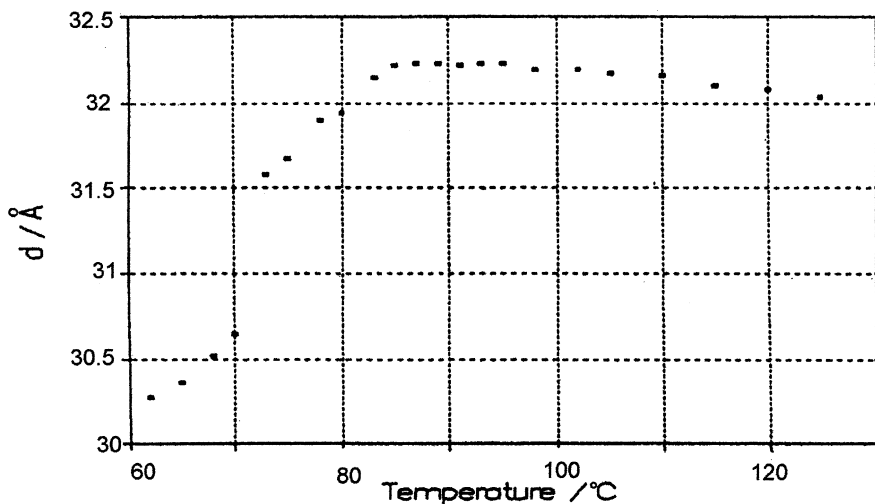
FIGURE 4 Temperature dependence of layer spacing for cyclic oligosiloxanes O6M8.

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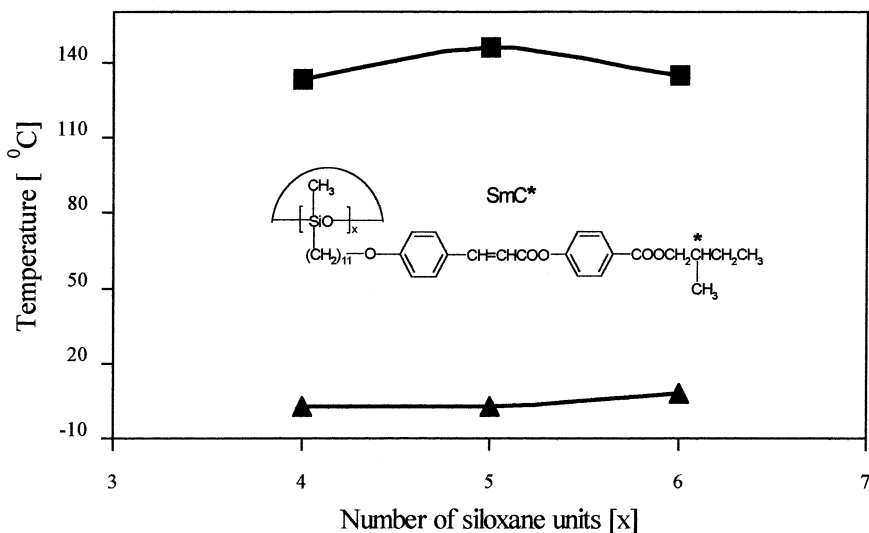
FIGURE 5 Influence of ring size on phase transition temperatures; (▲)-Glass transition temperatures, (■) Smectic C*-isotropic.
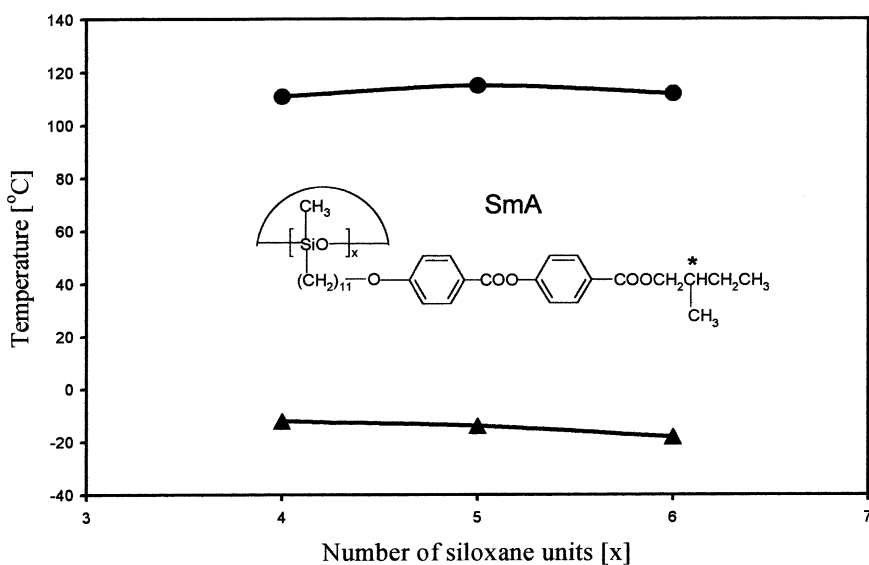
FIGURE 6 Influence of ring size on phase transition temperatures; (▲)-Glass transition temperatures, (●) Smectic A-isotropic.

decreasing glass transition temperatures depend on the size of ring of course, but also on the molecular weight of the mesogenic groups (Figs. 5–6).

So, in the case of cinnamic esters in mesogenic core, the glass transition temperatures increase with increasing size of the siloxane backbone.

By linking the siloxane ring to the mesogenic group with phenyl benzoate in core, decreasing glass transition temperatures are observed with increasing number of Si atoms in the siloxane ring.

A similar result was also observed with the changes of spacer length. The increasing number of C-atoms in the spacer length yields an increase in glass transition temperatures (O4M1–O4M3 or O6M1–O6M3) in contrast with the linear LC siloxane polymers [15].

The influence of the size of the siloxane ring on the distances of SmA or SmC* layers is relatively weak.

CONCLUSIONS

Three series of new side chain cyclic oligosiloxanes based on different mesogenic rigid cores with chiral end group have been synthesized and characterized. All of them exhibited enantiotropic smectic mesophases with monolayer structure. In particular, cyclic oligosiloxanes with cinnamoiloxyphenyl rigid core and (*S*)-2-methylbutyl chiral moiety display chiral smectic C mesophase, whereas the series with 4-benzoiloxyphenyl in mesogenic core form monolayer smectic A mesophase. Oligomers substituted by biphenyl of chiral chloroacids exhibit two liquid crystalline phases: chiral smectic C and smectic A.

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