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Cyclic versus linear siloxane liquid crystalline oligomers: phase behaviour

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The phase behaviour of cyclic and linear liquid crystalline polysiloxanes containing two different cholesteric mesogens is reported. The thermal properties of the synthesized monomers and oligomers were investigated by polarizing optical microscopy and differential scanning calorimetry. The influence of the structure of cyclic siloxane on the mesomorphic properties of cyclic liquid crystalline polysiloxanes is discussed. Similar trends in the thermal transitions of cyclic and linear compounds containing the same mesogenic composition were observed, though the cyclic oligomers showed poorer mesomorphic properties as compared with their linear analogues.

1. Introduction

The first cyclic liquid crystalline side chain siloxanes (CLCs) were reported in 1981 [1]. Since then, several reports on cholesteric CLCs have appeared, with special attention to their optical properties and potential applications as optical data storage and optical notch materials [2–4]. Some examples were published and compared with their linear analogues [5–7], showing that some of the properties of the cyclic compounds were markedly different from those of their linear analogues [6], while some exhibited similar thermal properties to the linear analogues [7, 8]. Computer simulations have predicted the formation of calamitic or discotic phases depending on the flexibility of the ring core and spacer groups [9, 10].

In this new work, a series of cyclic siloxane-based liquid crystalline oligomers containing two different cholesteric mesogens were prepared in the hope of obtaining outstanding optical properties including selective reflection and transmission of light, thermochromism and circular dichroism. In fact, the cyclic products had no such properties. At the same time a series of linear siloxane-based liquid crystalline oligomers containing the same two cholesterics mesogens were prepared. A similarity in the thermal transitions of the cyclic and linear compounds containing the same composition of mesogens was observed, though the cyclic polysiloxanes showed poorer mesomorphic properties than their linear analogues.

2. Experimental

2.1. *Materials*

Polymethylhydrosiloxane (PMHS) was purchased from Jilin Chemical Industry Co.; cyclic polymethylhydrosiloxane (CPMHS), cholesteryl acrylate (M1) and 4'-(2-methylbutoxy)biphenyl-4-yl 4-allyloxybenzoate (M2) were prepared according to literature procedures [11–13].

2.2. *Characterization*

A Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI, USA) was used to monitor the process of the polymerization reactions using cast films on salt plates. Thermal transitions were measured with a Perkin-Elmer DSC-7 instrument equipped with a PE 7300 data station with heating and cooling rates of $20^{\circ}\mathrm{C\,min}^{-1}$ under nitrogen. The textures of the liquid crystalline phases were observed with a Leitz optical polarizing microscope equipped with Mettler FP82 hot stage.

2.3. *Oligomer synthesis*

The structures of the cyclic and linear siloxane oligomers synthesized are shown in figure 1, and the polymerization experiments are summarized in table 1.

The two series of liquid crystalline oligomers containing M1 and M2 were prepared by graft

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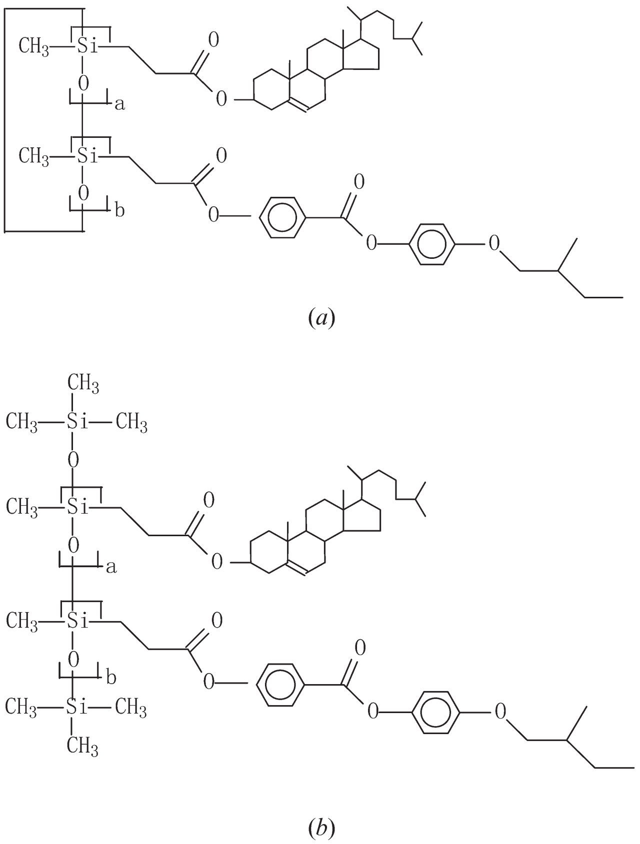


Figure 1. Structures of cyclic and linear polysiloxanes: (*a*) cyclic polysiloxanes ($a+b=4$); (*b*) Linear polysiloxanes ($a+b=7$).

copolymerization of mesogenic monomers upon PMHS or CPMHS in different proportions, using dry toluene as solvent and hydrogen hexachloroplatinate hydrate as catalyst. The reaction was carried out at 60–70°C until the IR spectra showed the disappearance of the Si–H absorption peak at $2160\,\mathrm{cm}^{-1}$.

3. Results and discussion

3.1. *Liquid crystal behaviour of monomers M1 and M2*

The thermal properties of monomers cholesteryl acrylate (M1) and 4′-(2-methylbutoxy)biphenyl-4-yl 4-allyloxy-benzoate (M2) were characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The phase transition temperatures, and the textures and main reflection colour of the monomers observed by POM are shown in table 2.

From the POM observations, M1 exhibited enantiotropic oily-streak texture, focal-conic texture and selective light reflection of the cholesteric phase during heating and cooling. When M1 was heated to the melting temperature, an obvious oily-streak texture and reflection colour appeared; the colour changed from red to blue between the melting temperature and the clearing point temperature, but the main reflection colour was blue. On cooling the sample from the isotropic melt, the focal-conic texture was formed, which readily transformed to oily-steak texture on shearing the sample, when the selective light reflection colour appeared. So M1 was selected to prepare cyclic siloxane liquid crystalline oligomers, which were expected to have outstanding optical properties.

M2 exhibited oily-streak texture, focal-conic texture and finger-print texture of the cholesteric phase, but showed no selective reflection of visible light during heating and cooling. When heated above the melting temperature, M2 displayed oily-streak texture, which did not change while heating to the clearing temperature. When cooled from isotropic phase, focal-conic

Table 1. Polymerization and thermal transitions of cyclic and linear oligomers.

Cyclic oligomer					Linear oligomer				
Oligomer	X_{M2}	$T_g{}^{a}$/°C	$T_{c1}{}^{bc}$/°C	$T_{c2}{}^{bd}$/°C	Oligomer	X_{M2}	$T_g{}^{a}$/°C	$T_{c1}{}^{bc}$/°C	$T_{c2}{}^{bd}$/°C
PC1	0.0	87.1	—	—	PL1	0.0	84.2	—	—
PC2	0.2	59.5	—	—	PL2	0.2	57.6	90	132
PC3	0.3	59.7	—	—	PL3	0.3	54.0	125	152
PC4	0.4	54.4	110	128	PL4	0.4	51.5	130	159
PC5	0.5	56.0	130	157	PL5	0.5	52.1	154	176
PC6	0.6	56.5	118	145	PL6	0.6	55.0	138	170
PC7	0.7	52.7	115	146	PL7	0.7	56.3	126	164
PC8	0.8	53.4	118	148	PL8	0.8	53.1	125	162
PC9	1.0	79.5	100	118	PL9	1.0	76.9	110	128

[a] Obtained by DSC.
[b] Obtained by POM.
[c] Temperature at which the birefringence begins to disappear.
[d] Temperature at which the birefringence completely disappeared.

Table 2. DSC and POM data of the monomers: Cr = solid, Ch = cholesteric, I = isotropic phase.

	DSC		POM	
Monomer	Heating/Cooling/°C	ΔT^{a}/°C	Texture	Main reflected colour
M1	Cr 79.6 Ch 124.3 I/I 119.1 Ch 25.5 Cr	44.7	Oily-streak Focal-conic	Blue
M2	Cr 114.4 Ch 207.4 I/I 197.4 Ch 63.3 Cr	93.0	Oily-streak Focal-conic Finger-print	—

[a] Mesomorphic temperature ranges.

texture was observed at first, turning to finger-print texture at the temperature slightly above crystallizing point; but this was merely an experimental observation under POM. For a monomer whose structure is similar to M2, but with the flexible spacer two carbon atoms longer, the transition from focal-conic to finger-print texture is significant in a thermodynamic sense: it exhibits an exothermic peak on the DSC curve. This suggests that the existence of finger-print texture strongly depends on the chemical structure of a liquid crystal compound. Photomicrographs of M1 and M2 are shown in figures 2 (*a*) and 2 (*b*).

3.2. *Liquid crystalline behaviour of oligomers*

The phase behaviour of cyclic siloxane oligomers with a low degree of polymerization is influenced by the molar ratio of side groups, similar to polymers of a higher degree of polymerization [5]. So in this work, we discuss the phase behaviour of the cyclic systems ignoring the fact that oligomeric CLCs inevitably consist of a mixture of different species with different compositions and distribution of the monomer units.

The thermal properties of the two series of cyclic and linear liquid crystalline polysiloxanes were determined by DSC and POM; their thermal transition data are showed in table 1. The DSC curves of all the oligomers showed only a glass transition, with no mesomorphic to isotropic transition, although six cyclic products and eight linear products exhibited clear birefringence under POM. Thus the T_g values in table 1 were obtained from DSC, and the clearing point temperatures T_c were obtained from POM. T_{c1} is the temperature at which the birefringence of the liquid crystalline oligomers began to disappear; T_{c2} is the temperature at which the birefringence completely disappeared. The various trends of the glass transition temperature T_g and the clearing temperature T_c, were only slightly different for cyclic and linear liquid crystalline polysiloxanes containing the same composition of mesogens.

The phase diagrams of the cyclic and linear systems established using POM are shown in figures 3 and 4, respectively. On the left-hand side of the cyclic system phase diagram (figure 3), a large isotropic region above a glassy solid phase was observed; unlike the large cholesteric mesophase region shown in the linear system phase diagram (figure 4). When the mole fraction of M2 was more than 0.4, the cyclic system exhibited a cholesteric mesophase region like the linear system, but

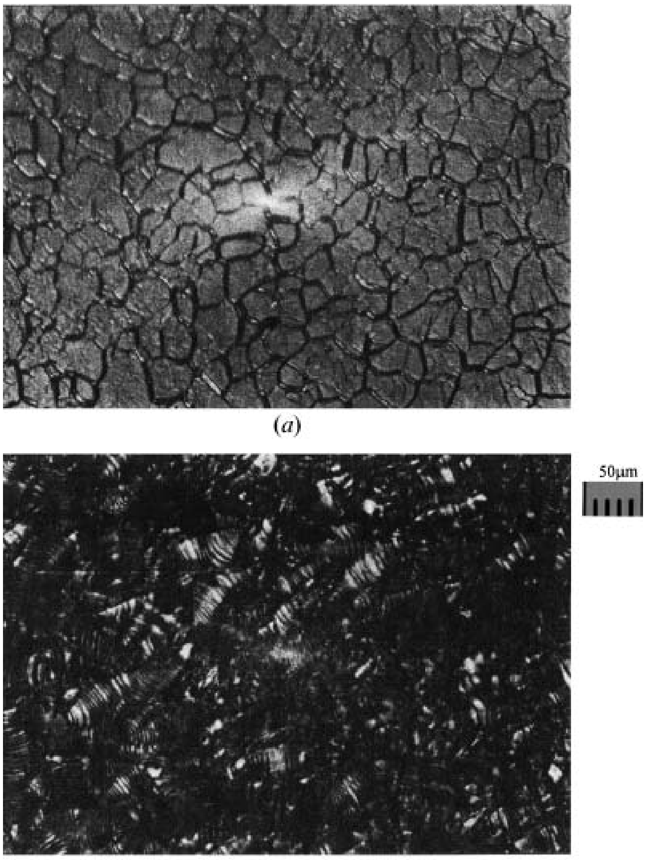


Figure 2. POM micrographs of monomers (200 ×): (*a*) oily-streak texture of M1 observed at 113°C; (*b*) finger-print texture of M2 observed at 71°C.

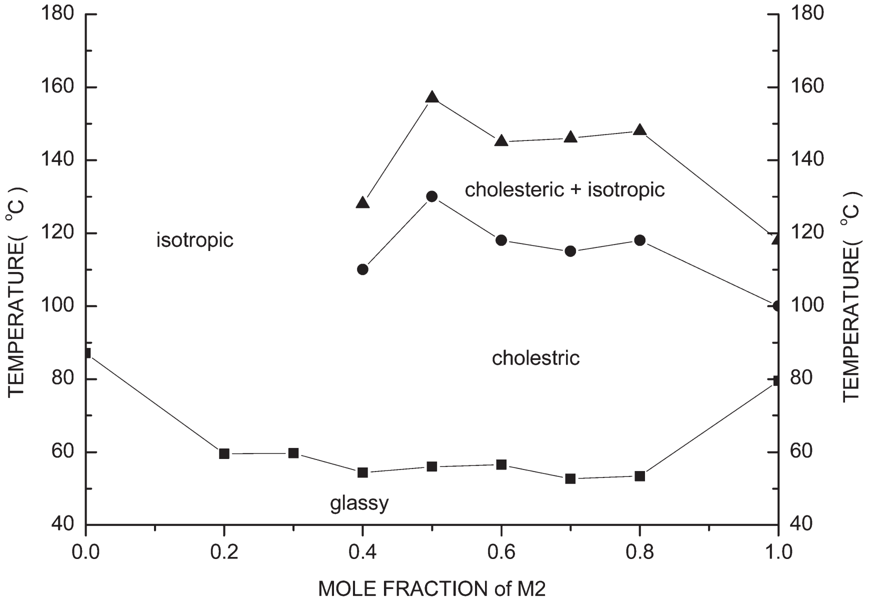


Figure 3. Phase diagram for cyclic siloxane oligomers.

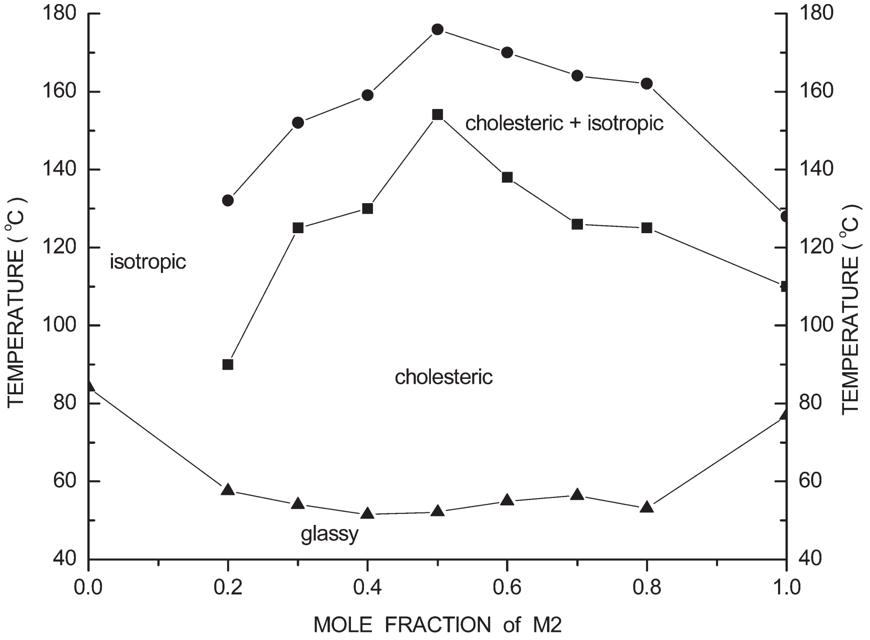
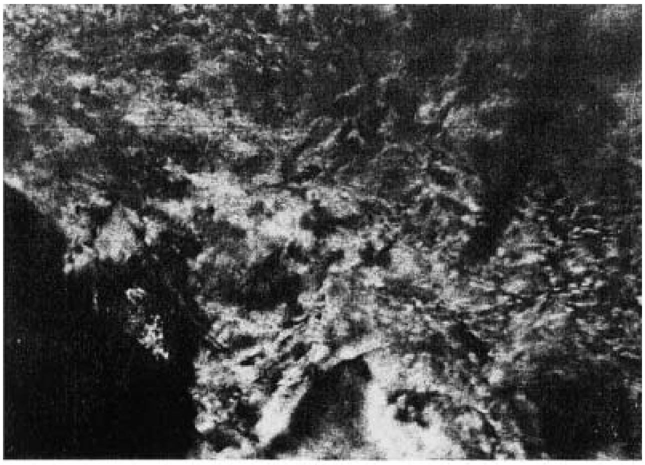


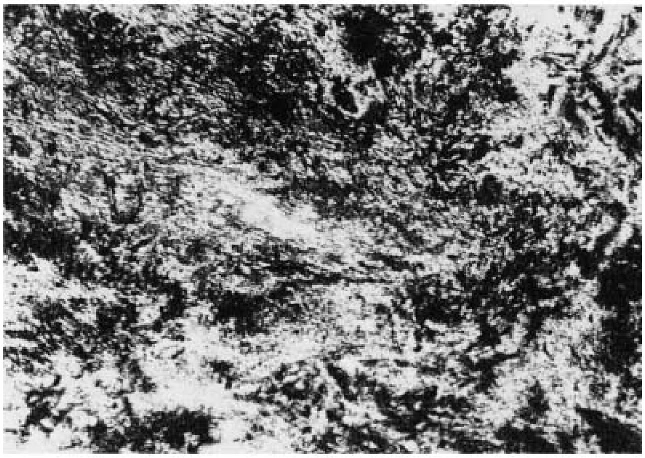
Figure 4. Phase diagram for linear siloxane oligomers.

the mesophase temperature regions of all the CLCs were narrower than those of the linear materials. Both cyclic and linear liquid crystalline polysiloxanes had a cholesteric–isotropic region above the cholesteric mesophase region; the T_{c1} and T_{c2} of the CLCs were lower, than for the linear materials.

Oligomers PC1 and PL1, having no M2 mesogenic units, exhibited no mesomorphic behaviour because of the shorter spacer length and greater steric hindrance of the bulky cholesteryl group (M1), which disturbed the orientation of the mesogen. PC2 and PC3 also showed no mesomorphic properties under POM, although PL2 and PL3 exhibited mesomorphic behaviour with mesophase regions ($\Delta T = T_{c2} - T_g$) of 74 and 98°C, respectively, due to the influence of the ring structure on the phase behaviour of the CLCs. The reason for this is that the rings with four Si–O repeat units of the cyclic siloxane backbone had a preponderant conformation and some degree of ring tension which disturbed the arrangement of the mesogenic units; the short spacer group of the bulky M1 cannot effectively decouple to the backbone to eliminate the influence of the ring conformational effect. However, the backbone of the linear siloxanes was more flexible and did not disturb the orientation of the mesogenic unit as much as the cyclic siloxanes did. The appearance of the mesomeric phases of the cyclic products PC4–PC9 was very similar to the phases obtained from their linear analogues: they all exhibited cholesteryl Grandjean texture, as shown in figures 5 (*a*) and 5 (*b*). With the decrease of M1 content, the degree of steric hindrance of M1 was also reduced, while the rod-like molecule of M2 was much easier to orient than the larger M1. Thus the structure of the siloxane backbone, as well as the nature of mesogenic units, affected the mesomorphic properties of CLCs.



(*a*)



(*b*)

Figure 5. POM micrographs of polymers (200 ×): (*a*) Grandjean texture of PC6 observed at 102°C; (*b*) Grandjean texture of PL6 observed at 107°C.

T_g is an important parameter in relation to the structures and properties of the polymers; it is affected by the mobility of polymer chain segments, and decreases with an increase in their mobility. In general, the T_g value of side chain liquid crystalline polymers is strongly influenced by the polymeric chain flexibility, molecular mass, the nature of the mesogenic group and the length of the spacer group. In this work, the T_g values of all the cyclic oligomers were higher than those of the corresponding linear materials. This type of T_g value coincided with the prediction of theoretical models which are based on the configurational entropy of cyclic and linear systems [14]. The additional rigidity of the siloxane ring hindered the motion of the polymer chain when passing through the glass transition. The flexibility difference between cyclic and linear siloxane backbones may be enhanced when the ring is constrained by attached bulky groups.

Although another research group has reported CLC mesophase–isotropic transition temperatures that are higher relative to the linear analogues [6], the result of our work was the opposite: the T_c of CLCs was lower than that of the linear materials.

In the cholesteric phase, a spatially periodic twisted helical structure is responsible for this effect: it selectively reflects visible light and exhibits brilliant colours if the cholesteric helix pitch coincides with the wavelength of visible light. It is known that the helical pitch of the cholesteric phase and the reflected colours depend mainly on the polymer structure, the temperature and the copolymer composition. Although M1 exhibited the colour of selective reflection of visible light, neither cyclic nor linear liquid crystalline polysiloxanes showed selectively visible light reflection of the cholesteric phase. This is because the pitchs of the cholesteric helix of the oligomers did not coincide with the wavelength of visible light.

4. Conclusion

Cyclic and linear liquid crystalline polysiloxanes containing two different cholesteric mesogens were synthesized. Similar trends in the thermal transitions of cyclic and linear compounds containing the same composition of mesogens were observed, although the cyclic oligomers showed poorer mesomorphic properties than their linear analogues. The structure of the siloxane backbone, as well as the nature of the mesogenic units affected the mesomorphic properties of the CLCs.

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