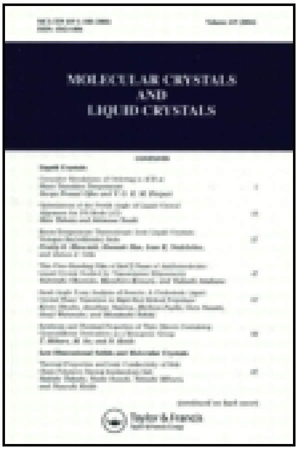

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Cyclic Versus Linear Siloxane Liquid Crystals: Phase Behavior and X-ray Diffraction Results

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Cyclic versus Linear Siloxane Liquid Crystals: Phase Behavior and X-ray Diffraction Results

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The phase behavior of cyclic and linear polysiloxanes containing biphenyl-4-allyloxybenzoate and cholesteryl-4-allyloxybenzoate mesogens is reported. The presence of the cholesterol-based mesogen was observed to induce layered packing structures for both linear and cyclic siloxane backbones. Differences in the mesophase behavior are discussed with respect to composition and type of siloxane. Small differences in the thermal transitions of cyclic and linear compounds containing the same composition of mesogens were observed. X-ray diffraction results are used to confirm the effect of composition on previously proposed packing models. Differences in the reflection spacings and intensity are discussed with regard to composition, temperature, and type of siloxane. Orientational differences between backbone type observed in aligned fibers are also discussed.

Keywords: liquid crystal, cholesteric, cyclic siloxane, X-ray diffraction

INTRODUCTION

Side-chain polymeric liquid crystalline materials based on flexible linear backbones with pendant mesogenic groups have been examined thoroughly during the past 20 years. The combination of mesogenic behavior with the macroscopic behavior

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of polymeric systems yields high molecular weight materials which exhibit anisotropic behavior. Although a complete understanding of the relationships that exist between spacer group, backbone, and mesogenic group has not been obtained, general rules have been developed predicting structure/property relationships.[1,2] A sufficiently long spacer group enables the rotational and translational motions of the mesogens to be dictated primarily by excluded volume interactions between nearest neighbor mesogens. The flexibility and degree of polymerization of the linear backbone influence the range of the mesophase region and the response of the mesogenic groups to applied magnetic and electric fields.

Recently, polymer and polymer liquid crystalline materials based on cyclic backbones have been examined. Cyclic polymers of a number of compounds have been examined up to 700 skeletal bonds.[3] Cyclic liquid crystalline compounds have been only recently examined and those systems, (polymethylhydrosiloxane[4,5,6] and polyphosphazene[7]), contained a small number (3–15) of repeat units. Computer simulations have predicted the formation of calamitic or discotic phases depending on the flexibility of both the ring core and the spacer group.[8,9] Weak coupling of the mesogens to the backbone (long spacer groups, flexible cores) resulted in conventional nematic phases while strong coupling (short spacer groups, rigid core) resulted in discotic-like phases formed by the splayed core and attached mesogens.

Recent results show a number of CLCS compounds based on a pentamethylcyclosiloxane ring[5] were calamitic. Derivatives of this system containing biphenyl-4′-allyloxybenzoate and cholesteryl-4′-allyloxybenzoate, shown in Figure 1(a), have been utilized in optical data storage materials[10,11] and optical notch filters.[12] Compounds containing between $0.1 < X_c < 0.5$ form cholesteric mesophases at elevated temperature. Glasses which exhibit selective reflection and reject circularly polarized light throughout the visible region can be formed by vitrification of the cholesteric mesophase into room temperature glasses. These glasses are optically transparent outside the selective reflection bandwidth.

Compounds within this limited composition range have also been preliminary examined using X-ray diffraction and electron microscopy techniques.[13] The packing of the two mesogens was found to be strongly dependent on the limited range of compositions. Changes in the type of molecular packing were attributed to the formation of regions where the cholesterol molecules are sterically limited in their ability to pack as seen previously for cholesterol-based homopolymers.[14,15] Preliminary packing schemes were proposed to account for the observed packing behavior as were general global shapes for the conformation of the pendant mesogenic groups relative to the siloxane ring.

To date, only one comparison of linear and cyclic backbones containing the same mesogens has been reported.[16] Compounds containing cyano-based mesogens on both linear and cyclic siloxane backbones exhibited strong differences in their phase behavior.[16] These markedly different phase properties were attributed to differences in the structure of the backbone. We report here on the phase behavior and X-ray diffraction results for linear and cyclic siloxane compounds throughout the entire phase diagram, $0.0 < X_c < 1.0$ as shown in Figure 1(a). A comparison of the thermal transitions for both types of compounds is discussed. X-ray diffraction was used to examine the interplay of the two mesogens in light of our recent work.[13]

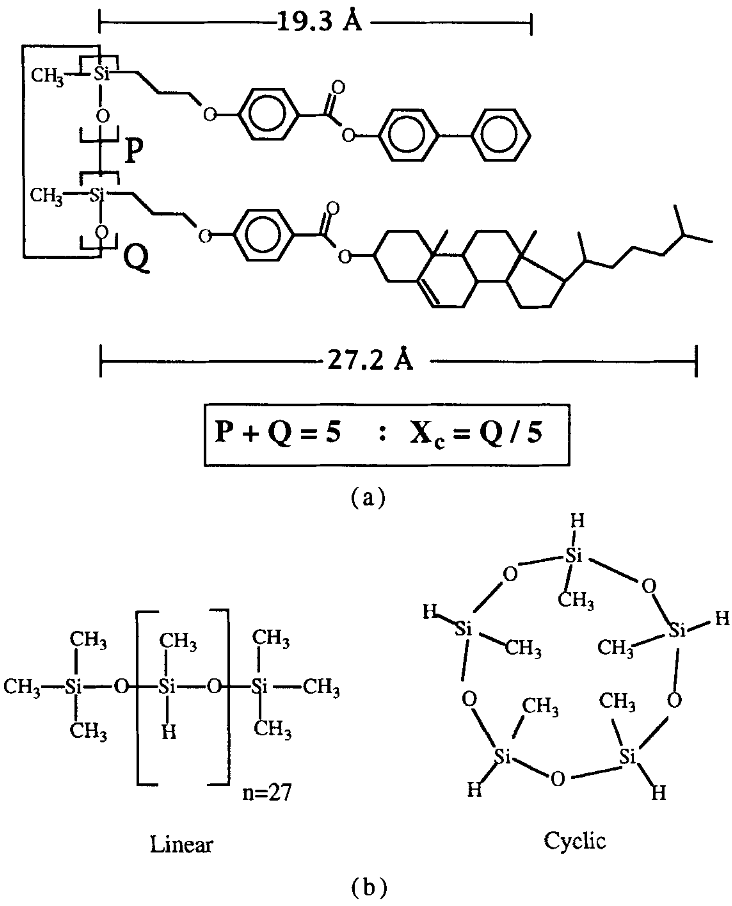

FIGURE 1 Structure of cyclic siloxane liquid crystalline compounds containing cholesteryl-4-allyloxybenzoate and biphenyl-4-allyloxybenzoate mesogens (a) and siloxane cores investigated (b).

Differences in *d*-spacings and intensities as a function of backgone type, composition, and temperature are discussed. Orientation differences in fibers drawn from linear and cyclic compounds are examined.

EXPERIMENTAL

FTIR spectra were recorded on an Perkin Elmer 1725X FT-IR spectrometer and H^1 NMR spectra were recorded on a Bruker AM-360. UV-VIS spectra were recorded on either a Lambda 9 UV-VIS spectrometer or a Lambda 4B UV-VIS spectrometer equipped with an integrating sphere for specular reflection measurements. DSC measurements were recorded on a Perkin Elmer DSC-2C or a Dupont 910 DSC taken from the second heating or cooling scans. Values are reported using a 10°C/min heating rate. Polarized optical microscopy was performed on a Nikon Optiphot-Pol microscope equipped with a Mettler FP82HT hot stage. X-ray diffraction was performed on a Rigaku RU-300 (12 kW) generator using CuKα radiation (graphite monochromator). Samples were run in the transmission mode using a Warhus (flat-film) camera at various sample-to-film distances. Some elevated temperature diffraction measurements were performed at the Cornell High Energy Synchrotron Source (CHESS) on the A-1 beam line. Optical densities were extracted from films using a Joyce-Loebl Scandig 3 densitometer. Fibers were drawn from the mesophase using tweezers. Room temperature diffraction was performed on fibers or films quenched from the mesophase in air to a glassy state.

SYNTHESIS

Allyloxybenzoic acid was synthesized as reported.[17] Esterification of this compound onto cholesterol or hydroxybiphenyl was performed with *N*,*N*′-dichlohexylcarbodiimide and dimethylaminopyridine using a previously reported method.[18] Attachment to the cyclic and linear polymethylsiloxanes (Huls America) shown in Figure 1(b) was performed using standard hydrosilation chemistry with a dicyclopentadienylplatinum(II) chloride catalyst. Both siloxanes were vacuum distilled prior to use. The platinum catalyst was synthesized per the method of Drew.[19]

Hydrosilation reactions were carried out in toluene at 80–90°C under argon. Reaction progress was followed by monitoring the disappearance of the Si-H stretch at 2155 cm^{-1} using FTIR spectroscopy. Upon completion, the reaction solution was filtered into methanol which caused the product to precipitate. This was done repeatedly until TLC[20] showed no residual alkene remained in the product. FTIR, H^1 NMR, and elemental analysis confirmed the starting structures of both mesogens and the platinum catalyst. H^1 NMR confirmed the statistical integrity of the final products with respect to the starting composition. A small amount of propene elimination, a side reaction present when using allyloxy leader groups discussed by Kreuzer,[5] was observed with H^1 NMR for all siloxane compounds.

RESULTS AND DISCUSSION

The thermal transitions of the eight cyclic and six linear compounds synthesized are shown in Table I. The phase diagram for the cyclic system is shown in Figure 2. On the left side of the phase diagram, a large cholesteric mesophase region above a glassy solid phase was observed. POM revealed characteristic Grandjean oily streaks[21] in the mesophase region. The thermal transitions and reflection wavelengths for compounds C15, C30, and C50 agree with previously reported data.[5] A slight difference of these values with those reported previously[13] is attributed to a distribution of ring sizes[12] and the presence of unreacted alkene[22,23] in the latter. There was little dependence of the selective reflection wavelength with temperature. Compound C00 exhibited a lower temperature crystalline phase above which a nematic mesophase was present. Extensive DSC measurements indicate two melting peaks upon heating separated by a recrystallization endotherm as listed in Table I. Only one recrystallization was observed on cooling at 92°C. Within the

TABLE I

Thermal and optical properties of cyclic and linear polysiloxanes with various compositions of biphenyl-4-allyloxybenzoate and cholesteryl-4-allyloxybenzoate mesogens

Cyclic Compounds

Compound	X_{chol}	Thermal Transitions	λ_{max} (nm)[1]
C00	0.00	k_1 115 k_2 135 n 175 i	n/a
C15	0.15	g 47 n* 180 i	1050
C30	0.30	g 50 n* 208 i	647
C50	0.50	g 50 n* 220 i	514
C60	0.60	g 50 S_A 120 n* 230 i	n/a
C70	0.70	g 61 S_A 200 n* 245 i	n/a
C85	0.85	g 60 S_A 210 n* 244 i	n/a
C100	1.00	g 61 S_A 228 n* 246 i	n/a

Linear Compounds

Compound	X_{chol}	Thermal Transitions (°C)	λ_{max}
L00	0.00	k 120 n 170 i	n/a
L25	0.25	g 50 n* 210 i	red
L50	0.50	g 62 n* 230 i	blue
L65	0.65	g 65 S 190 n* 228 i	n/a
L75	0.75	g 60 S >230 dec	n/a
L100	1.00	g 72 S > 250 dec	n/a

k-crystalline; n-nematic; n*-cholesteric; S_A-smectic-A; i-isotropic; g-glassy; dec-decomposed; n/a-not applicable

[1] - selective reflection wavelengths measured from room temperature glasses

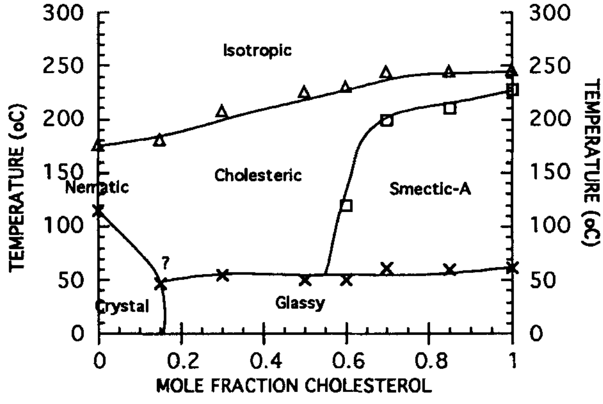

FIGURE 2 Phase diagram for cyclic siloxane compounds shown in Figure 1.

mesophase, POM revealed only a nematic phase (consistent with a cholesteric with an infinite pitch) and no signs of other textures appearing upon cooling to room temperature.

Compounds containing more than 50% cholesterol formed a lower temperature smectic-A phase in addition to a narrow upper temperature cholesteric phase. The selective reflection wavelengths were very dependent on temperature for these compounds. Large homeotropic areas, characteristic of smectic-A phases, were observed with POM. The clearing temperature rose with increasing amounts of cholesterol as did the glass transition temperatures.

The linear analogs, listed in Table I, exhibited similar glass transition and clearing transitions as their cyclic counterparts. Compounds L65, L75, and L100 exhibited undetermined smectic phases as indicated by POM. Based on the phase diagram reported for the cyclic compounds and the similarities between thermal transitions, this phase is most likely a smectic-A phase. X-ray diffraction results, discussed later, confirm this behavior. Decomposition set in before a clearing temperature could be reached for compounds L75 and L100 and there was no indication of the higher temperature cholesteric phase present for the cyclic compounds. The glass transition and clearing temperatures were only slightly different for linear and cyclic analogs containing the same composition of mesogens. Large differences in the mesophase-isotropic transitions observed previously with the cyano-based mesogens,[16] attributed to the trimethylsilyl end groups of the linear polysiloxane, were not observed. These differences were shown to be strongly dependent on the nature of the mesogenic group attached. As packing among liquid crystalline polymeric systems has been shown to be dependent on the mesogens and backbone, this may indicate the relative strength of either of the components in the molecular packing geometry.

One, two, or three sharp low-angle reflections and a diffuse wide angle reflection were present in the unaligned diffraction patterns of both the cyclic and linear compounds as shown in Figure 3(a). Fiber patterns showed marked differences in the orientation of the mesogens relative to the fiber axis as shown in Figure 3(b). Diffusion patterns from linear compounds indicated the mesogens were perpendicular to the fiber axis as low-angle reflections were observed on the equator. Contrary to this, diffraction patterns from cyclic compounds of the same composition revealed meridional alignment of the low-angle reflections. Meridional alignment of the wide-angle reflections for the linear compounds is typical for layered (smectic) polymer liquid crystalline structures. The extended polymer backbones, lying parallel to the draw direction, promote the slipping of the smectic layers along the fiber direction.[24] The unusual ability of the cyclic compounds to draw fibers with meridional alignment of the mesogens has been discussed previously.[13] Fibers, readily drawn from the cholesteric phase, were more difficult to form from the smectic phase. Cyclic compounds drew fibers much easier and longer than linear analogs containing the same composition.

Also present to varying degrees in the aligned diffraction patterns were periodic diffuse reflections characteristic of short-range order in liquid crystalline polymers.[25,26,27] These periodic reflections, previously attributed to higher order reflections,[13] may reflect a tendency of the molecules to form strings of aligned

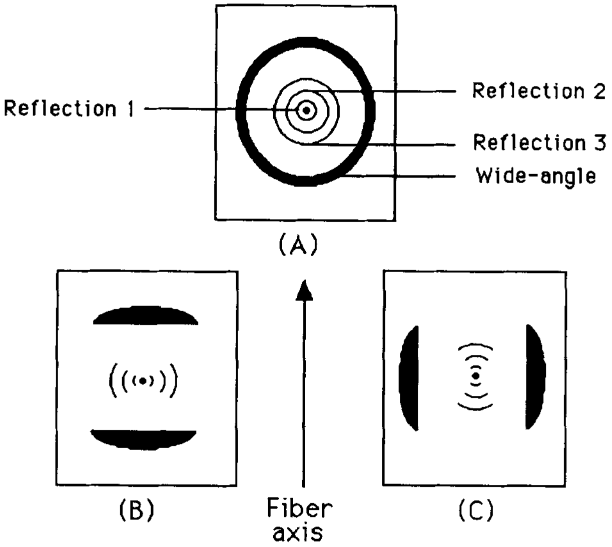

FIGURE 3 Schematic of unaligned diffraction patterns of cyclic and linear compounds (a) and fiber diffraction patterns of linear (b) and cyclic (c) compounds. The fiber axis is indicated by the arrow.

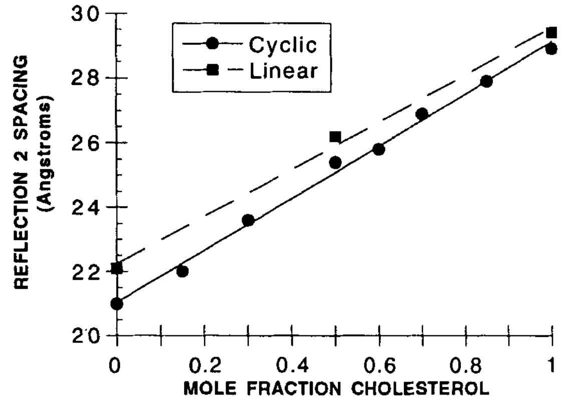

FIGURE 4 Reflection 2 spacings as a function of composition for linear and cyclic compounds.

molecules.[28,29,30] These reflections were much sharper in the cyclic compounds and as these compounds were easier to draw, this may indicate the drawing ability of the cyclic compounds arises due to the formation of intertwined molecules lying parallel to the fiber direction.

The appearance, spacing, and intensity of the observed reflections were greatly dependent on composition. The wide-angle spacings increased from 5–6.3 Å as the amount of cholesterol was increased due to its larger cylindrical volume. These reflections are attributed to cyclindrical lateral interactions among mesogens.[31] The *d*-spacing of reflection 2 varied linearly with composition for both cyclic and linear compounds as shown in Figure 4. *d*-spacings of 21 to 30 Å were larger than those calculated from the extended molecular lengths of the two molecules (shown in

Figure 1(a)). The linear slopes in Figure 4 are identical to the predicted slope indicating the mesogens are statistically packing as a single entity. The measured *d*-spacings, however, were larger than those predicted by the statistical packing and may indicate a contribution of the siloxane in the repeat distance. The linear compounds, possessing slightly larger *d*-spacings than their cyclic analogs, exhibited the same linear dependence on composition. Reflection 1, around 50 Å, varied little in spacing with composition for both linear and cyclic compounds. Compounds C00, C15, L00, and L25 did not exhibit reflection 1. Compounds C85, C100, and L100 also exhibited reflection 3, 19 Å, whose origin will be explained when discussing the origin of reflections 1 and 2.

There was little broadening or weakening of reflection 2 upon entering the smectic phase. Figure 5 shows little difference in the shape of this reflection for both the cholesteric and smectic phase of compound C60. This was also true when comparing the diffraction patterns of compounds C30 and C50 in their cholesteric phase to those from compounds C60 and C70 in their smectic phases. This is indicative of a layered packing scheme consistent with previous results.[15,32] Instead of the typical twisted nematic model, a more layered-like microscopic structure, heloidical on the macroscopic scale, would seem pertinent for these compounds.

These three reflections have been attributed previously to two types of molecular packing.[15,33] Based on the similarities between the reflections in the smectic and cholesteric phases, reflection 2 was attributed to a mixed region of mesogens in a bilayer-like packing scheme as shown in Figure 6(a). Reflection 1 has been attributed to regions of partially overlapped cholesterol molecules as shown in Figure 6(b). At low cholesterol contents, the mixture of mesogens behave statistically as one as evidenced by the linear dependence of reflection 2 on composition. As more cholesterol molecules are added, regions which are predominantly cholesterol form due to steric hindrances resulting from the larger molecular volume of this mesogen. Both types of packing are present in compounds with $X_c > 0.3$ as indicated by the appearance of both reflection 1 and 2. This packing instability has been observed previously for liquid crystalline homopolymers with cholesterol mesogens attached with varying spacer group lengths. Compounds containing short leader groups only

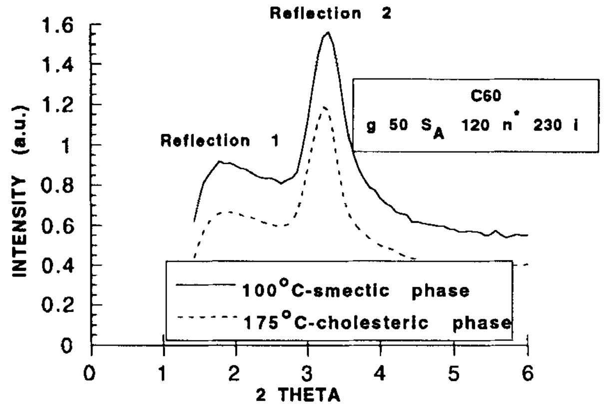

FIGURE 5 Intensities of reflection 1 and 2 for compound C60 in the cholesteric and smectic phases.

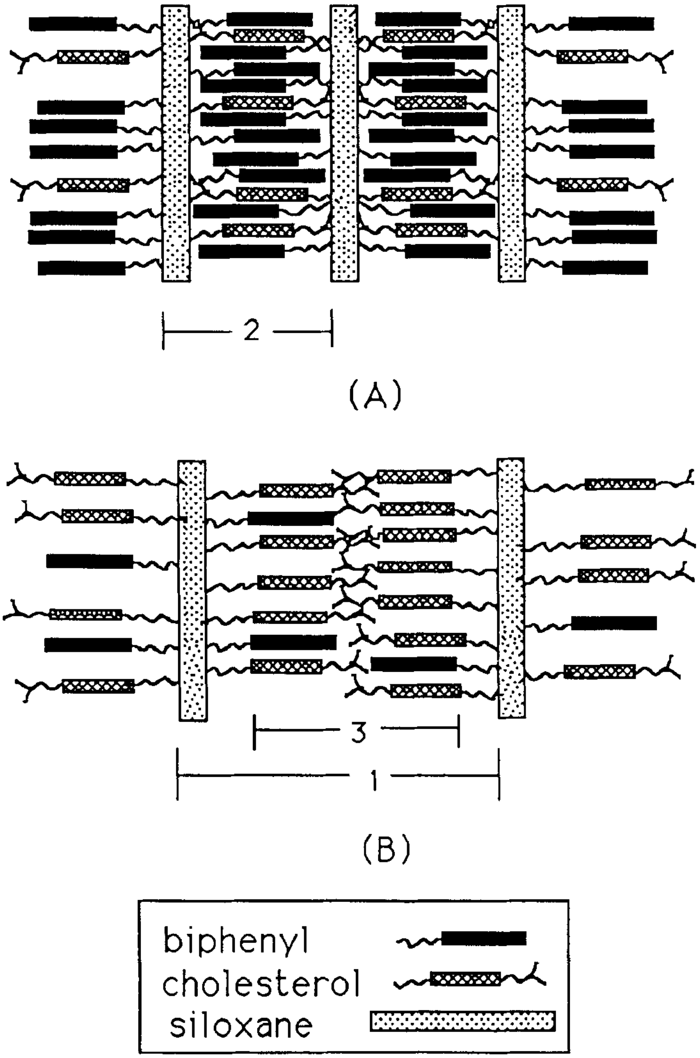

FIGURE 6 Packing scheme for the biphenyl-rich compounds showing extensive association of the mesogens (a). Above 30% cholesterol, the packing scheme in (b) is present and consists of partially overlapped cholesteryl mesogens. The proportion of packing in (b) to (a) changes with composition and temperature.

exhibited reflection 1 while those possessing long leader groups exhibited only reflection 2. Both reflections were observed with compounds with medium length leader groups. The observed dependence on composition for these compounds leads to interesting speculations about possible domain formation and microphase separation among mesogens. Computer calculations investigating the compatibility of these two mesogens with themselves and the siloxane core are underway. Compounds C85, C100, and L100 also exhibited reflection 3, ~19 Å, which arises due to the overlap of these sterically hindered molecules as shown in Figure 6(b).

Above 30% cholesterol, the intensity of reflection 1 steadily increased relative to the intensity of reflection 2 indicating a change in the proportion of the two packing schemes. This was true for both the linear and cyclic compounds as shown in Figure 7. It is not clear whether this behavior is due to differences in chemical compatibility among the mesogens or are solely driven by steric hindrances. No difference in the intensity of reflection 3 was observed for compounds C85 and C100. The intensity ratio was higher for the linear compounds at a given composition indicating a higher percentage of interdigitated molecules are present in the cyclic-based compounds. This is peculiar as the close proximity of the five attachment sites per cyclic core should decrease packing efficiency among sterically hindered molecules.

Elevated temperature diffraction also revealed trends with regard to *d*-spacings and intensities of these three reflections. There was no change in the spacing of reflection 2 for both the cyclic and linear compounds throughout the mesophase region. This was also true at the smectic-cholesteric transitions of compounds C60,

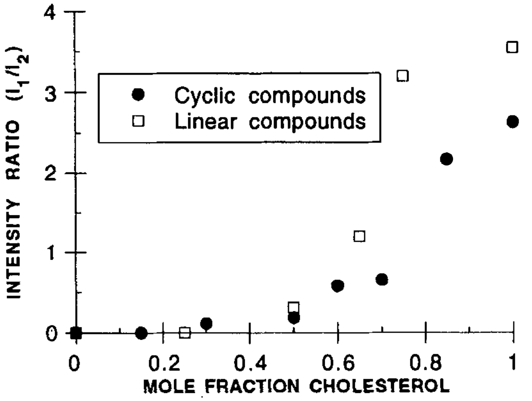

FIGURE 7 Ratio of the intensity of reflection 1 to reflection 2 as a function of composition for the cyclic and linear compounds.

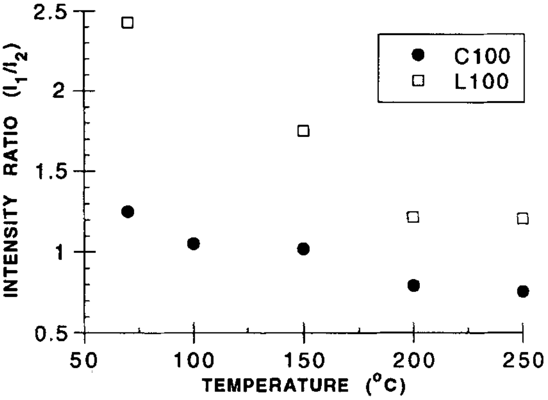

FIGURE 8 Ratio of the intensity of reflection 1 to reflection 2 as a function of temperature for the cyclic and linear compounds.

C70, C85, and C100. A slight shortening of reflection 1 was observed for the cyclic compounds as temperature was increased. The wide-angle *d*-spacings also slightly increased with temperature for both sets of compounds. Most revealing however, was the dependence of intensity ratio discussed earlier with temperature. Linear and cyclic analogs exhibit similar behavior, both decreasing with temperature as shown in Figure 8. The decrease was a combination of an increase in reflection 2's intensity and a decrease in reflection 1's intensity. Thus, more regions as shown in Figure 6(a) form at the expense of Figure 6(b) regions. The increase in thermal energy is thought to overcome some of the energy limitations of the sterically hindered cholesterol molecules. The opposite behavior was observed upon cooling.

CONCLUSIONS

The phase behavior of a previously exploited class of cholesteric cyclic copolysiloxanes was examined throughout the phase diagram. There was little difference in the thermal transitions of analogs possessing either cyclic or linear backbones. Large orientational differences were observed in aligned fibers; cyclic compounds aligned with their mesogens along the draw direction while linear compounds aligned with their backbones along the draw direction. Cholesterol-rich compounds exhibited a tendency to layer pack. Two packing schemes, dependent on composition, were examined with respect to backbone type and temperature.

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