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The mesophase structure of a series of sixteen cholesterol-based liquid crystalline materials based on cyclosiloxane backbones is examined. The co-existence of two layer types (full and partial interdigitation of cholesterol mesogens) in the mesophase is examined as a function of ring size, composition, and spacer length. The relative X-ray intensities from each layer type are discussed as a function of these variables. An increase in the ring size and cholesterol composition, and a decrease in the spacer group all result in more partially interdigitated packing. Molecular modeling calculations performed on the mesogens and macromolecules examine relative differences in the orientational relationships and flexibility of mesogens.

Keywords: Liquid crystal, cholesterol, interdigitation, X-ray diffraction, cyclic siloxane, molecular modeling

1. INTRODUCTION

Cholesteric side-chain liquid crystalline polymers (LCP) are of technological importance because of their unique optical properties.[1] Iridescent, glassy films produced by quenching the aligned Grandjean texture present in this class of materials have been utilized in information storage and optical devices.[2–5] Synthesis of new cholesteric LCP's from esters of cholesterol has largely been unsuccessful as smectic rather than cholesteric liquid crystals are typically formed. However, it is possible to form cholesteric mesophases by co-polymerization of a cholesteryl ester with a nematogen

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or by employing a nonsteroidal chiral mesogen. In both phases sharp X-ray reflections at low scattering angles ($2\theta = 2°-4°$) indicate a strong tendency for cholesterol-based molecules to layer pack.[1]

Several authors[6-8] have observed distinct X-ray reflections from two separate repeat units in both smectic and cholesteric liquid crystal phases of LCP systems. The appearance of one or two reflections was found to be dependent upon the length of the spacer attaching the mesogen to the polymer and the flexibility of the polymer backbone. Each reflection has been attributed to a layered structure that corresponds to a different degree of mesogen interdigitation (Fig. 1). In systems with long spacers

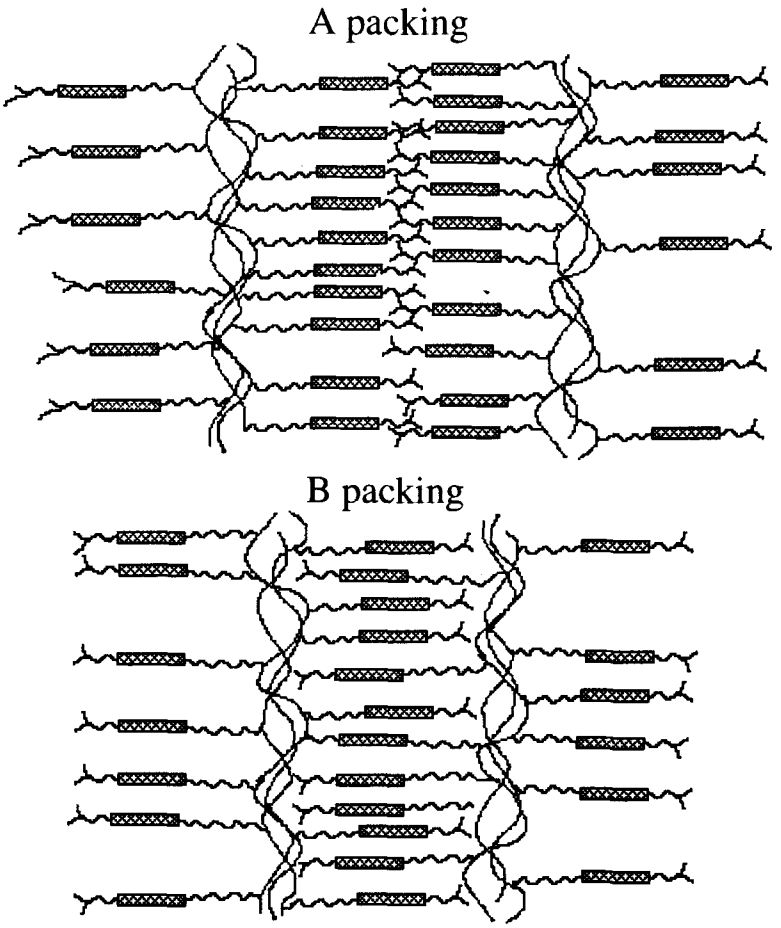

FIGURE 1 Schematic representation of the two types of packing observed for cholesterol-based liquid crystalline systems depending on the length of the spacer group. Short leader systems do not allow full interdigitation as the aliphatic tails provide steric hindrance. This gives rise to a low angle spacing slightly less than twice the molecular length (*A* packing). Long spacers allow the mesogens to fully interdigitate, giving rise to a layer length approximately equal to the mesogen length (*B* packing). Both layer packing schemes coexist for moderate flexibility systems.

a reflection corresponding approximately to the length of an extended mesogen (including spacer) was observed (referred to as *B*-packing). A decoupling of the cooperative motions between mesogens and the polymer backbone, controlled primarily by the longer spacers, allowed the mesogens to fully interdigitate. A second reflection corresponding to partial interdigitation of mesogens was observed in materials with relatively short spacers (referred to as *A*-packing). In these compounds, full overlap of mesogens was precluded by steric interactions between aliphatic tails. Large r.m.s. anisotropic thermal vibrations in the terminal methyl groups of the aliphatic tails have been observed in the single crystal X-ray structures of cholesteryl esters. These large thermal vibrations give rise to a loosely packed structure proximate to the aliphatic tails.[9] Both reflections (*A* and *B*) were observed in the liquid crystalline phase of compounds with intermediate length spacer groups. This coexistence of layer packing was observed in both the smectic and cholesteric mesophases.[6,7]

Similar structures in the mesophase of a variety of cholesteryl ester-substituted cyclic and linear siloxane-based liquid crystalline compounds were observed in a recent study.[10] Two types of layer packing were proposed based upon two X-ray reflections present in diffraction patterns of both smectic and cholesteric mesophases. The relative amounts of the two layered packing schemes (i.e., partially and fully interdigitated mesogens) were determined by comparing the intensities from each X-ray reflection. The packing of a variety of compounds was studied as a function of mesogen composition, backbone type, and temperature which provided insight into their influence on the mesophase structure.

We report in this paper a study of the mesophase structure of sixteen mesogen-substituted cyclosiloxane liquid crystals.[11] In particular, the coexistence of two distinctly packed layers which results from fully and partially interdigitated mesogens is examined. This extension of the previous work examines the effects of cyclosiloxane ring size, spacer group length and substituents on *d*-spacings and packing efficiency by X-ray diffraction. Molecular modeling calculations offer a qualitative explanation of the observed differences in packing.

2. EXPERIMENTAL PROCEDURES

The synthesis and thermal characterization of all compounds have been published previously.[11] The compounds studied are LC mesogen-substituted tetramethylhydrocyclotetrasiloxane and pentamethylhydrocyclopentasiloxane (referred to as D4 and D5, respectively). The LC mesogens were based on either cholesterol or biphenyl. Cyclosiloxane cores substituted with either 100% cholesterol mesogens or a statistical 50/50 biphenyl/cholesterol mixture were examined. Four spacer groups, vinylbenzoate, allyloxybenzoate, penteneoxybenzoate, and octeneoxybenzoate were individually used to attach the mesogens to the cyclosiloxane core. Chemical structure drawings are given in Figure 2. Thermal transitions of the compounds are listed in Table 1.

X-ray diffraction experiments were undertaken with graphite monochromated CuKα radiation ($\lambda = 1.5418$ Å) from a Rigaku Rotaflex RU-300 rotating anode X-ray source operated at 40 kV/300 mA (12 kW). An evacuated Statton camera with sample-to-film distances of 50, 72.9, and 170 mm was used to record the diffraction patterns.

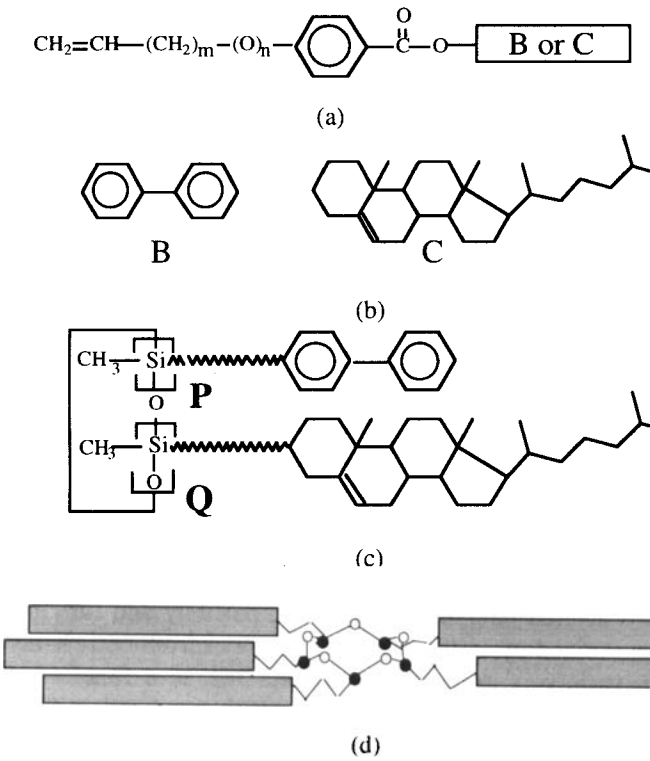

FIGURE 2 Chemical structure of the spacer groups (a) mesogens (b) substituted cyclosiloxane rings (c) and a possible conformation of the entire molecule (d). Three of the spacer groups contain an oxygen atom ($n = 1$) while the shorter does not ($n = 0$).

TABLE 1

Nomenclature and thermal transitions of cyclosiloxane LC compounds

Name	Ring size ($P + Q$)	Spacer group*	% Cholesterol	Thermal Transitions (°C)
5VC	5	Vinyl ($m = 0, n = 0$)	100	$g\,76\,S_A\,247\,i$
5AC	5	Allyloxy ($m = 1$, $n = 1$)	100	$g\,61\,S_A\,228\,n^*\,246\,i$
5PC	5	Pentyloxy ($m = 3$, $n = 1$)	100	$g\,50\,S_A\,255\,i$
5OC	5	Octyloxt ($m = 6$, $n = 1$)	100	$g\,49\,S_C^*\,100\,S_A\,252\,i$
4VC	4	Vinyl	100	$g\,100\,S_A\,232\,i$
4AC	4	Allyloxy	100	$g\,76\,S_A\,270\,n^*\,277\,i$
4PC	4	Pentyloxy	100	$g\,58\,S_A\,263\,i$
4OC	4	Octyloxy	100	$g\,55\,S_C^*\,100\,S_A\,246\,i$
5VCB	5	Vinyl	50	$g\,80\,n^*\,204\,i$
5ACB	5	Allyloxy	50	$g\,50\,n^*\,220\,i$
5PCB	5	Pentyloxy	50	$g\,41\,S_C^*\,130\,S_A\,198\,n^*\,228\,i$
5OCB	5	Octyloxy	50	$g\,26\,S_A\,199\,n^*\,209\,i$
4VCB	4	Vinyl	50	$g\,75\,n^*\,204\,i$
4ACB	4	Allyloxy	50	$g\,57\,n^*\,237\,i$
4PCB	4	Pentyloxy	50	$g\,35\,n^*\,220\,i$
4OCB	4	Octyloxy	50	$g\,30\,S_A\,204\,n^*\,210\,i$

* m and n refer to Figure 2

g-glassy; n^* cholesteric; S_A smectic A; S_C^* chiral smectic C; i isotropic

X-ray exposure times ranged from two to twenty four hours. Thin film samples were prepared by heating material between two Teflon coated plates followed by an air quench to room temperature. Some compounds were packed into quartz capillaries for examination directly in the mesophase. Capillary samples were heated in a micro-heater placed inside the Statton camera. These samples were exposed to X-rays subsequent to a two hour equilibration at the temperature of interest. Densitometry was performed on the flat films with a Molecular Dynamics Personal Densitometer running ImageQuant software. Intensity data were obtained from films with an optical density less than 1.5. Background corrections were performed using same-time exposed film.

Molecular modeling calculations were performed with the SYBYL and Quanta/CHARMm force fields and parameters with a crystal energy minimization program (CREAM). CREAM optimizes the interactions between rigid molecules by minimizing the intermolecular energy of the system. An exp(6) intermolecular potential function was used to model the intermolecular interactions. The TRIPOS force field parameters for Si atom interactions were modified to better agree with available experimental and theoretical data.[12] SYBYL and CREAM software were run on an IBM RS/6000 Powerstation 340. Quanta/CHARMm software was run on a Silicon Graphics IRIS 4D/420VGX workstation. Molecular dynamics simulation times varied from 20 to 150 picoseconds (ps), with a 0.001 ps time step. Heating rates were 25–50 K/ps.

3. RESULTS AND DISCUSSION

A typical intensity versus 2θ plot for an unaligned sample is shown in Figure 3. The data exhibit three distinct features. The strong low angle peak ("*A*" in Figure 3) at $2\theta \approx 2°$ corresponds to a *d*-spacing of approximately twice the extended substituent length. This reflection is attributed to the packing of sterically hindered cholesterol mesogens in which the aliphatic tails of proximate mesogens only partially overlap (see *A* packing, Figure 1). A second reflection ("*B*" in Figure 3), observed at $2\theta \approx 4°$, corresponds to fully interdigitated mesogens packed in lamellae (see *B* packing, Figure 1). At wider angles ($2\theta \approx 17°$), a broad reflection (denoted as *C* in Figure 3) is observed corresponding to the average lateral spacing between neighboring substituents. Summarized in Table 2 are the measured and predicted *d*-spacings (predicted spacings measured on models of fully extended substituents) for the sixteen compounds studied. The calculated length for mixed (50/50) mesogen compounds is based upon a rule of mixtures model. X-ray reflection spacings reported in Table 2 were obtained from samples quenched to room temperature.

The measured *d*-spacings from reflection *B* increased with increasing spacer group length. The measured *d*-spacings were larger than the calculated *d*-spacings for all compounds except 5PC, 4PC, and 4OC. Both the predicted and calculated *d*-spacings of the mixed mesogen compounds were shorter than those for the all-cholesterol compounds due to the presence of shorter biphenyl-based mesogens. Differences between the predicted and calculated *d*-spacings were much larger for these mixed mesogen compounds. The significance of this difference is unclear although many previously reported studies of non-polar mesogens indicate measured *d*-spacings

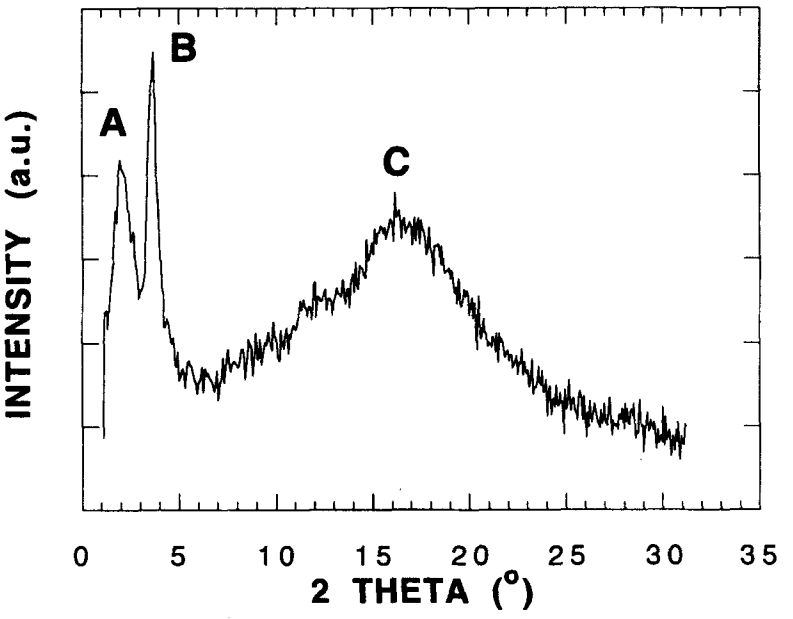

FIGURE 3 X-ray diffraction pattern from compound 4VCB, showing two layer reflections, *A* and *B*, and one broad wide angle reflection, *C*.

TABLE 2

Observed and predicted *d*-spacings

Name	d_{pred} (Å)	*A* spacing (Å)	*B* spacing (Å)	*C* spacing (Å)
5VC	24.7	46.0	26.2	6.0
5AC	27.2	50.0	28.9	5.8
5PC	29.7	–	29.3	5.2
5OC	32.7	–	34.0	5.0
4VC	24.7	46.7	25.9	5.5
4AC	27.2	49.9	28.2	5.2
4PC	29.7	–	29.1	5.3
4OC	32.7	–	32.1	5.0
5VCB	20.9	44.1	24.5	5.2
5ACB	23.0	46.9	25.6	5.0
5PCB	25.6	–	26.0	4.8
5OCB	28.9	–	32.1	4.7
4VCB	20.9	42.9	23.9	5.1
4ACB	23.0		25.0	4.9
4PCB	25.6	–	26.4	4.8
4OCB	28.9	–	31.2	4.7

typically 5–10% shorter than the predicted lengths due to fluctuations in mesogen orientation within lamellae.[13] The predominantly larger measured *d*-spacings observed here and their strong dependence on structure may suggest the ring backbone is contributing to these spacings. For a given composition, measured *d*-spacings were also

slightly smaller in the D4-based compounds for all four spacer group lengths compared with the D5 component. Except for compounds 5OC, 4OC, and 5PCB, each of which exhibit a chiral smectic $C(S_C^*)$ phase, no significant temperature dependence of this reflection was observed. The dependence of this spacing for compound 5PCB is illustrated in Figure 4. The d-spacing increased with temperature up to the S_C^* to S_A phase transition temperature as the arrangement of molecules within lamellae transformed from a tilted to a non-tilted structure.[14]

The d-spacing corresponding to the wide angle reflection (C) decreased with increasing spacer group length (Figure 5). These values were obtained from room temperature samples and no distinction between the S_A, S_C^*, or n^* phases was made. This may be due to an increase in the mobility of mesogens attached with long spacer groups resulting in more efficiently packed substituents. Wide angle spacings were smaller in the D4-based and mixed mesogen compounds. The smaller spacings in the D4 systems are a result of fewer unfavorable steric interactions between pendant mesogens. This decrease in mesogen crowding results in more efficiently packed mesogens and therefore smaller intermolecular distances.

Molecular dynamics (MD) simulations were undertaken with the SYBYL molecular modeling software and a TRIPOS force field[12] to examine the effect of spacer group length on the intermolecular spacing of substitutents in 4VC and 4OC. A dynamics simulation at 400 K was completed on each molecule (each with four pendant mesogens). The simulation was performed inside a cylindrically symmetric surface of aromatic carbon atoms, (i.e., a tube of graphite) to provide a boundary condition on the single molecule during the simulation. Total simulation times ranged between 20–30 ps for each system. The intermolecular distances between atoms in the spacer, tetracyclic core of cholesterol, and aliphatic tail were monitored during the simulation. Results

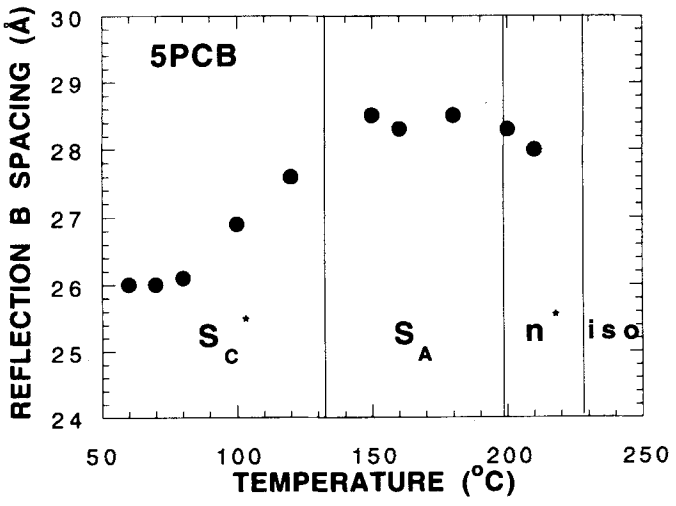

FIGURE 4 Elevated temperature diffraction data for compound 5PCB showing the change in the layer spacing (B) as a function of temperature for a $S_C^* \longrightarrow S_A$ phase transition.

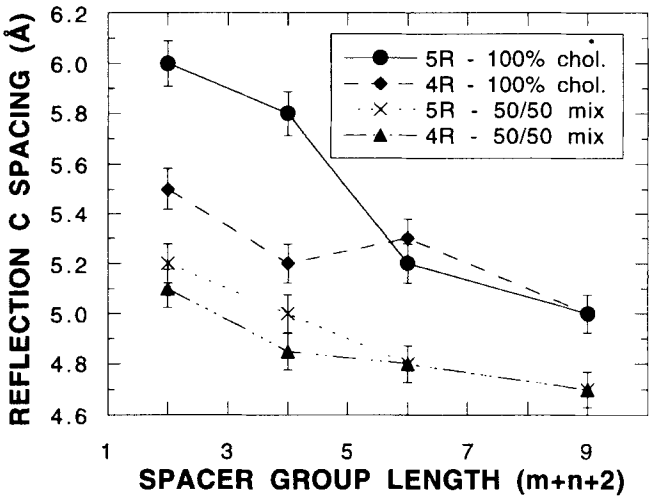

FIGURE 5 Spacing of reflection *C* as a function of spacer group length for D4- and D5-based compounds. *m* and *n* refer to Figure 2.

indicate that the 4OC substituents pack approximately 15% closer (on average) than the 4VC substituents during the simulation. Of the three regions in the substituent that were monitored the atoms in the spacer groups were packed most closely.

For the mixed mesogen systems, the replacement of bulky cholesterol mesogens with smaller biphenyl mesogens results in a change in lateral spacings. Smaller *C* spacings were observed in these materials compared to the all-cholesterol systems. To investigate the effect of molecular size/shape on the optimum separation distance between molecules, molecular mechanics calculations on pairs of biphenyl, biphenyl/cholesterol and cholesterol-based mesogens (each with allyloxybenzoate spacer groups) were undertaken with CREAM. The separation distance and orientational relationship of mesogen pairs was optimized by minimizing the intermolecular energy between molecules. Calculations indicate the minimum energy separation distance for two biphenyl-based mesogens was 4.0 Å–4.5 Å. The optimum spacing between biphenyl- and cholesteryl-based mesogens was 4.5 Å–5.0 Å. The optimum spacing between two cholesteryl-based mesogens was 5.5 Å–6.0 Å. The trends as well as the absolute values of the calculated separation distances agree well with the observed spacings in the mixed mesogen and all-cholesterol mesogen systems.

Reflection *A* was observed only in compounds with relatively short spacers (i.e., vinylbenzoate and allyloxybenzoate: see Figure 6). The *d*-spacing for reflection *A* corresponds to approximately twice the extended mesogen length *minus* the length of one aliphatic tail unit. The presence of this reflection supports the proposed packing of partially interdigitated molecules as shown in Figure 1 (packing type *A*). The absence of this reflection for the longer spacers indicates that their increased flexibility is sufficient to overcome steric interactions causing reflection *A*. The vinylbenzoate spacer group compounds also consistently exhibit a significantly higher intensity for reflection

A than the allyloxybenzoate compounds. The appearance of an X-ray reflection from each packing type suggests that the relative amounts of each can be examined by comparison of the relative X-ray intensities from each reflection.

The efficiency of packing in ordered host materials may also affect temporal stability as loosely packed structures possessing more 'free volume' may allow more molecular motion to occur at lower temperatures. The molecular environment in which NLO chromophores reside dictates the temporal stability of an induced optical signal obtained after alignment by an electric field. An increase in the void volume of host materials (heating above the glass transition temperature of an amorphous polymer system) causes increased molecular motion and therefore an increased rate of thermal relaxation of the aligned chromophores. Similar cholesterol-based cyclosiloxanes have shown promise as carriers for second order nonlinear optical (NLO) chromophores.[15–18] It is therefore important to understand the different types of packing present and how various changes in the molecular architecture affect each packing.

To examine differences in packing efficiency for this possible class of host materials, the ratio of intensities from reflections *A* and *B* was compared to evaluate the relative amounts of the two packing types. An increase in free volume in packing type *A* is suggested by the loosely packed aliphatic tail region. The packing ratios (PR), defined as the ratio of the intensities of reflections *A* to *B*, are listed in Table 3. As previously stated, compounds with long spacer groups (pentyloxybenzoate and octyloxybenzoate) did not exhibit reflection *A* and therefore have packing ratios equal to zero. In all materials, the shorter spacer group compounds exhibited the largest packing ratios indicating the prevalence of partially interdigitated, sterically hindered packing. This packing ratio serves as a means of identifying the type of structure in the mesophase. At the two extremes, a packing ratio of zero indicates fully interdigitated mesogens (typically those compounds with long spacers), while a packing ratio of infinity

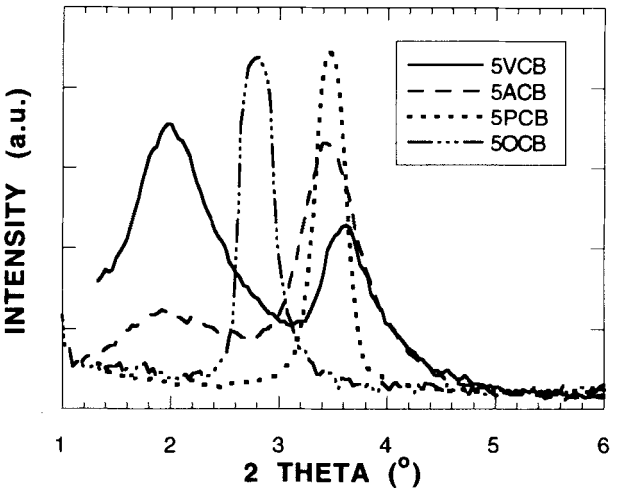

FIGURE 6 Intensity of reflections *A* and *B* as a function of spacer group for ring size and composition. The longest two spacer group compounds do not exhibit reflection *A*.

indicates completely non-interdigitated mesogens (typically those compounds with short spacers). In general, the ratio decreased with temperature as observed previously.[10] Compounds possessing multiple phases and both *A* and *B* reflections (5AC and 4AC) did not show abrupt changes when passing from one phase to another. As expected the intensity of both reflections was weaker in the n^* phase than in the smectic phase.

The D4-based compounds exhibited lower packing ratios than D5-based compounds, as shown in Figure 7 and Table 3. This increase in interdigitated packing arises from fewer steric interactions in the D4 system. To examine the flexibility differences between systems, molecular dynamics (MD) simulations of substituted D4 and D5 cyclosiloxanes were undertaken.[12] MD simulations were run on three previously proposed low energy conformations of the D4- and D5-based compounds.[19] D4 and D5 siloxanes were substituted with cholesterol and biphenyl-like mesogens attached with vinyl spacer groups. Molecules were simulated both *in vacuo* and within a periodic boundary array of 27 molecules. The flexibility of the mesogens with respect to the cyclosiloxane core was probed by examining the range of the O-Si-$C_{(\text{first atom in spacer})}$-$C_{(\text{second atom in spacer})}$ dihedral angle in each compound. This dihedral angle is one of many examined in each compound during the MD simulation. The range in this dihedral angle variation for each substituent was averaged to yield a single value for each compound. This dihedral angle range value was on average 3.5 times larger in the substituted D4 systems than in the substituted D5 systems. This result indicates an increase in mesogen flexibility with respect to the cyclosiloxane core in the D4 system which is attributable to fewer steric interactions. Mixed mesogen systems also exhibit smaller packing ratios than their 100% cholesteryl counterparts, indicating that the biphenyl-based mesogens undergo less hinderance in their end-to-end packing. When systematically examined as a function of composition, it has been observed that a larger percentage of these smaller mesogens allows more overlap of the cholesterol mesogens thereby reducing the packing ratio.[10] Diffraction experiments on all-biphenyl-based

TABLE 3

Packing ratios

100% cholesterol compounds			
Compound	Packing ratio	Compound	Packing ratio
5VC	4.2	4VC	2.2
5AC	1.1	4AC	1.0
5PC	0.0	4PC	0.0
5OC	0.0	4OC	0.0
50/50 cholesterol/biphenyl compounds			
Compound	Packing ratio	Compound	Packing ratio
5VCB	1.3	4VCB	0.7
5ACB	0.5	4ACB	0.0
5PCB	0.0	4PCB	0.0
5OCB	0.0	4OCB	0.0

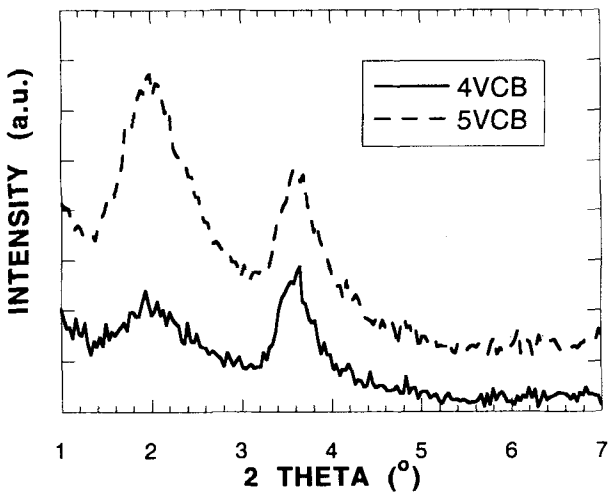

FIGURE 7 Intensity of reflections *A* and *B* for D4- and D5-based liquid crystalline siloxanes. The larger *A* reflection relative to the *B* reflection for the D5-based compound correlates to poorer packing efficiency among mesogens.

compounds indicate the absence of reflection *A* regardless of the spacer group or ring size.[10]

4. SUMMARY

X-ray diffraction and molecular modeling were used to investigate the mesophase order of sixteen substituted cyclosiloxane LC's. Compounds with varying ring size, spacer group lengths, and mesogen compositions were examined. Two distinct types of packing, as evidenced by two separate reflections coexist in both cholesteric and smectic LC phases. The intensities of these reflections were used to characterize differences in packing among the sixteen compounds. Mixed mesogens compounds were more interdigitated than the all-cholesterol compounds. Longer spacer groups allowed full interdigitation of the cholesterol molecules. D4-based compounds packed more efficiently than the D5-based materials because of fewer steric interactions. Molecular mechanics calculations indicate a distinct trend in the optimum separation distances of cholesteryl, biphenyl and mixed mesogen pairs. These results correlate well with the trends observed in the wide angle spacing data. Molecular dynamics calculations indicate increased flexibility in the D4-based systems in qualitative agreement with X-ray diffraction results.

Acknowledgements

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