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Molecular dynamics simulations of siloxane-based side chain liquid crystalline polymers

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Molecular dynamics simulations have been performed to study the intramolecular interactions of biphenyl ({B}) and cholesterol ({C}) substituents on linear oligomeric siloxanes. These interactions are of interest due to the liquid crystalline behaviour of these materials. Molecules with alternating diblock and triblock substituent arrangements were examined, as were unmixed substituents. The orientational behaviour of the mesogens and the stability of {B}–{B}, {C}–{C}, and {B}–{C} interactions were characterized by an order parameter for the mesogens as a function of simulation time. Results indicate that the {C}–{C} interaction is the strongest, with the {B}–{B} and {B}–{C} interactions being weaker. However, the arrangement of {B} and {C} mesogens in the different molecules strongly influenced the level of mesogen ordering. The flexibilities of the siloxane backbone and the spacer groups used to attach the mesogens give the mesogens a wide range of motion, allowing them to find energetically favourable arrangements and moderate to high order parameters. Published by Elsevier Science Ltd.

(Keywords: molecular dynamics; liquid crystal; siloxane; cholesterol; biphenyl)

INTRODUCTION

Side chain liquid crystalline materials have been a subject of recent interest for application in non-linear optical devices[1,2] and in optical filters and reflectors[3,4]. In particular, the liquid crystalline behaviour of biphenyl and cholesterol mesogens attached to a variety of siloxane molecules has been studied[5–11]. The liquid crystalline behaviour of substituted cyclic pentasiloxane has been examined with a variety of experimental techniques[5,7,10]. X-ray diffraction experiments on this and similar materials yielded spacings consistent with a model where mesogens from neighbouring molecules form either interdigitated, partially interdigitated, or non-interdigitated structures, depending on the temperature[12] and/or mole fraction of biphenyl and cholesterol[7]. In previous computer modelling studies, molecular mechanics (MM) and molecular dynamics (MD) were used to study the intermolecular interactions of the mesogens in biphenyl- and cholesterol-substituted cyclic pentasiloxane[5–9]. These studies showed favourable mesogen interactions and a tendency toward packing structures consistent with X-ray data. Biphenyl and cholesterol substituted linear polysiloxane was also found to exhibit liquid crystalline behaviour. X-ray diffraction data indicated a packing structure similar to that for substituted cyclic siloxane[7]. Intermolecular interactions between mesogens (interdigitation) have been characterized for cyclic molecules, and it has been assumed that these results hold for linear molecules as well. However, the nature of interactions between mesogens that may occur within a single substituted linear siloxane molecule have not been characterized. An *in vacuo* molecular dynamics study of purely intramolecular interactions between biphenyl and cholesterol mesogens in substituted linear polysiloxane is described in this paper.

The molecular dynamics computational method (MD) is used to simulate the behaviour of molecules by calculating atomic motions within the molecules as a function of time and temperature. The starting point for this method is computing the forces on the atoms by considering terms due to bond stretching, angle bending, out of plane bending, torsion angles, and van der Waals non-bonded interactions. Additional force terms that describe other effects may be added if necessary (for example, Coulombic interactions). These forces are then used in Newton's second law to determine an acceleration for each atom in the molecule over a small time interval (~1 fs). The velocities of atoms are then scaled to the desired simulation temperature according to:

$$3Nk_BT = \sum m_i v_i^2 \quad (1)$$

where N is the total number of atoms, k_B is Boltzmann's constant, T is the temperature, and m_i and v_i are the mass and velocity, respectively, of the ith atom. These scaled velocities are used to update the position of the

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atoms at the end of the time interval. Then, the forces are recalculated for the new atomic positions and the process is repeated. See, for example, reference 13 for a complete discussion.

METHODS

Construction of molecules and MM and MD calculations were performed with the SYBYL[14] molecular modelling program version 6.01 on an IBM RS/6000 Powerstation 340 workstation. An augmented/modified version of the Tripos force-field was used for all calculations. The base Tripos force-field has been used extensively and validated for a wide range of compounds[15]. However, parameters for siloxane are not included, so these had to be added to the force-field.

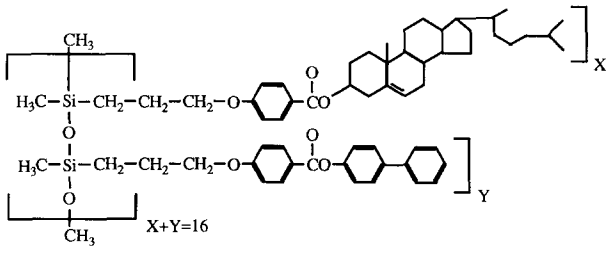

Figure 1 General structure of linear substituted siloxane with (X) cholesterol and (Y) biphenyl mesogens

These were taken from original work by Grigoras and Lane[16,17] and from the Cambridge Structural Database. In addition, the parameters for biphenyl were modified to produce the correct energy *versus* plane inclination profile. These were based on values determined previously from semi-empirical calculations[18]. The parameters used in the current research differed in the following ways: C_{ar}–C_{ar}–C_{ar}–C_{ar} single bond torsion force constant = 0.95 kcal/mol · deg^2 (Farmer *et al.*: 1.00); C_{ar}–C_{ar} single bond stretch constant = 500 kcal/mol · Å^2 (Farmer *et al.*: 633.5); C_{ar}–C_{ar} single bond equilibrium value = 1.51 Å (Farmer *et al.*: 1.48). The modified force-field produced orientational results that were significantly different from those obtained using the unmodified Tripos force-field, and these results are more consistent with experimental data. Specifically, very poor biphenyl alignment was observed when the default Tripos force-field was used. This is contrary to experimental results which show a liquid crystalline phase for biphenyl substituted siloxanes. The modified force-field produced a biphenyl alignment which would be consistent with a liquid crystalline phase.

Coulombic interactions were not considered in the simulations. Previous studies on cholesterol and siloxanes indicated that inclusion of these interactions may introduce more error than simply omitting them[5]. The Verlet method[19] was used to calculate velocities and positions at the midpoint of the MD time interval. Since the time step must be small compared to the highest frequency motion in the molecule, a 1 fs time step was

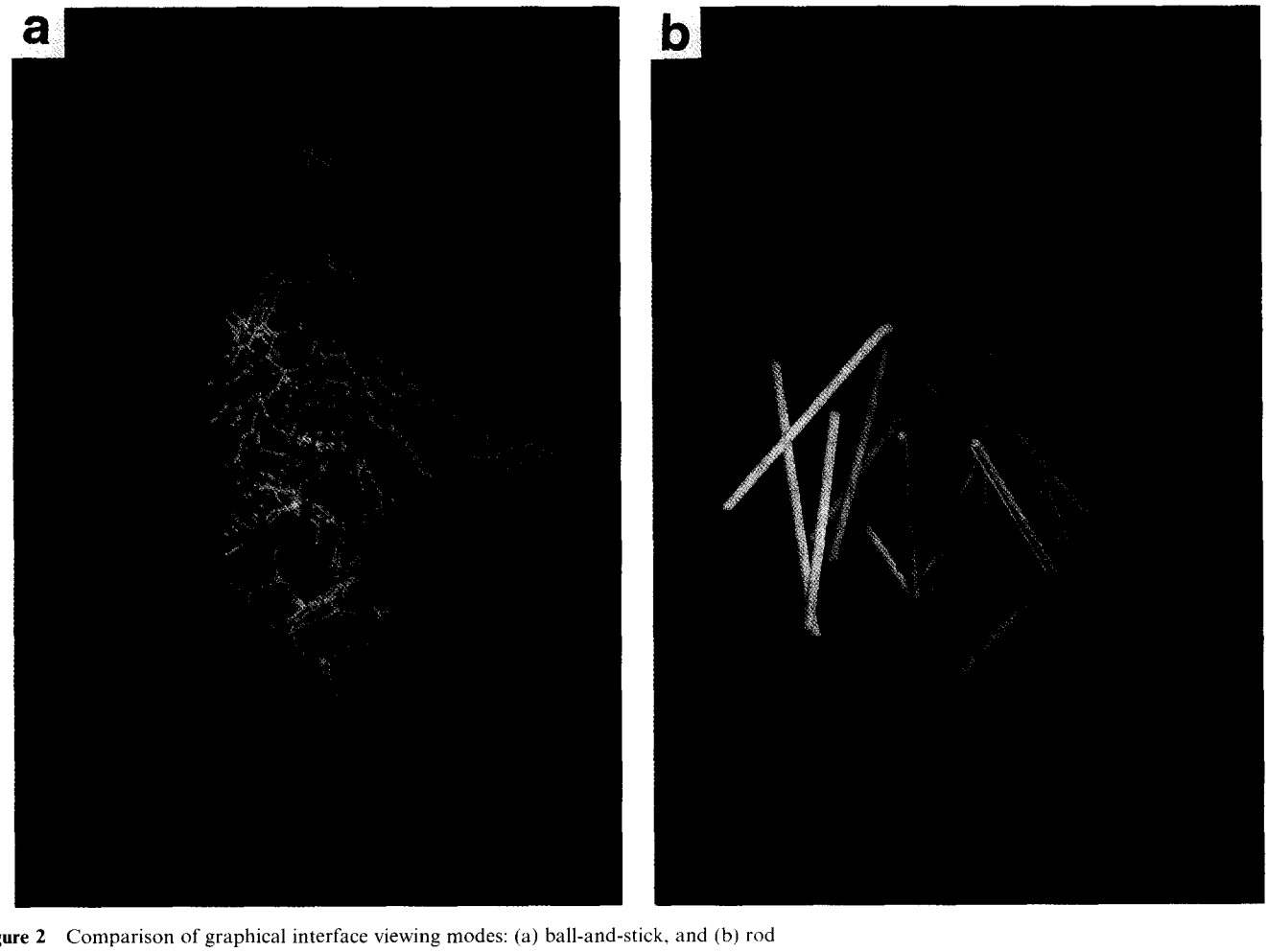

Figure 2 Comparison of graphical interface viewing modes: (a) ball-and-stick, and (b) rod

used. No constraints on motion were applied during MD.

Five linear siloxane molecules, with various combinations of biphenyl ({B}) and cholesterol ({C}) substituents were constructed to study the degree of alignment that could be achieved by the mesogens in different combinations. The mesogens were attached to the siloxane by a flexible allyloxybenzoate 'spacer' group that served to increase the range of motion of the mesogens. This spacer has been used in previous modelling and experimental studies. Each molecule had 16 siloxane repeat units with 16 mesogens attached in an isotactic arrangement. The combinations of mesogens considered were: all biphenyl, all cholesterol, {B}–{C} diblock (8{B}–8{C}), {C}–{B}–{C} triblock (5{C}–6{B}–5{C}), and alternating {B}/{C}. *Figure 1* shows the general form of these molecules.

All molecules were constructed with the siloxane backbone having an initial all plus-gauche conformation, resulting in a three-fold helical structure. This initial arrangement provides the most disperse distribution of mesogens. A molecular mechanics energy minimization was carried out on each molecule. This consisted of an initial non-derivative based Simplex procedure to remove close contacts within the structure, followed by a Powell procedure, iterated until the change in energy per iteration was less than 0.05 kcal/mol. This minimization removed very high energy atomic arrangements which would prevent the system from reaching equilibrium in a reasonable simulation time. The particular initial conformational state and energy that the molecules converged to was not very important, since it quickly disappeared during the MD simulation.

The MD simulations began with a heating stage, with the temperature increased from 0 to 300 K in 50 K increments of 50 fs duration. The molecules were then simulated at 300 K for 200 ps. An equilibration period, during which the substituents rearranged, followed the heating stage. During this time, the mesogens moved into energetically favourable arrangements. This rearrangement appeared to tail off by 150 ps in all of the molecules considered. Calculations were performed for molecules in vacuum, at constant temperature.

An order parameter is a measure of the alignment of the mesogens with a director and is one of the characteristic measures of liquid crystallinity[20]. The director is defined as the average direction vector for all of the mesogens. For current purposes, the direction vector for a given mesogen was taken to point from the first carbon atom after the spacer to the outermost carbon atom in the mesogen. The angle between each mesogen direction vector and the director was measured (α_i), and the order parameter was computed from:

$$S = \tfrac{1}{2}(3\langle\cos^2\alpha_i\rangle - 1) \qquad (2)$$

The order parameter was calculated for each of the molecules as a function of MD simulation time. As defined, the order parameter has the properties that $S = 0$ for a randomly oriented distribution of mesogens, $S = 1$ for perfect alignment of mesogens, and $S = -1/2$ for a random distribution of mesogens in a plane normal to the director. There are various ways of grouping mesogens for consideration in the mixed mesogen molecules ({B}–{C} diblock, {C}–{B}–{C} triblock, and alternating {B}/{C}). Those which were computed include: biphenyl mesogens only, cholesterol mesogens only, all mesogens, and individual blocks of cholesterol in the {C}–{B}–{C} triblock molecule.

All MD simulations were fully atomistic. However, as a tool to visualize the associations between mesogens, a 'rod' viewing mode was used. In this greatly simplified viewing mode, each mesogen is depicted as a bar representing the direction vector. Similarly, the spacer group is simplified by removing hydrogen atoms and replacing the phenyl group with a single virtual bond. The siloxane backbone is stripped to only silicon and oxygen atoms by removing the methyl side groups. This viewing mode is a great improvement over ball and stick or space-filling models for visualizing alignment of mesogens. *Figure 2* shows a comparison of the ball-and-stick and rod viewing modes for the {C}–{B}–{C} triblock molecule after 200 ps of MD simulation.

SIMULATION RESULTS

All-biphenyl molecule

The all-biphenyl molecule showed stable groups of aligned mesogens throughout the MD simulation. *Figure 3* shows orthogonal rod depictions of this molecule after 200 ps of MD simulation. At 200 ps, several aligned groups were observed with 2–4 biphenyl mesogens each. In the early equilibration stages of the

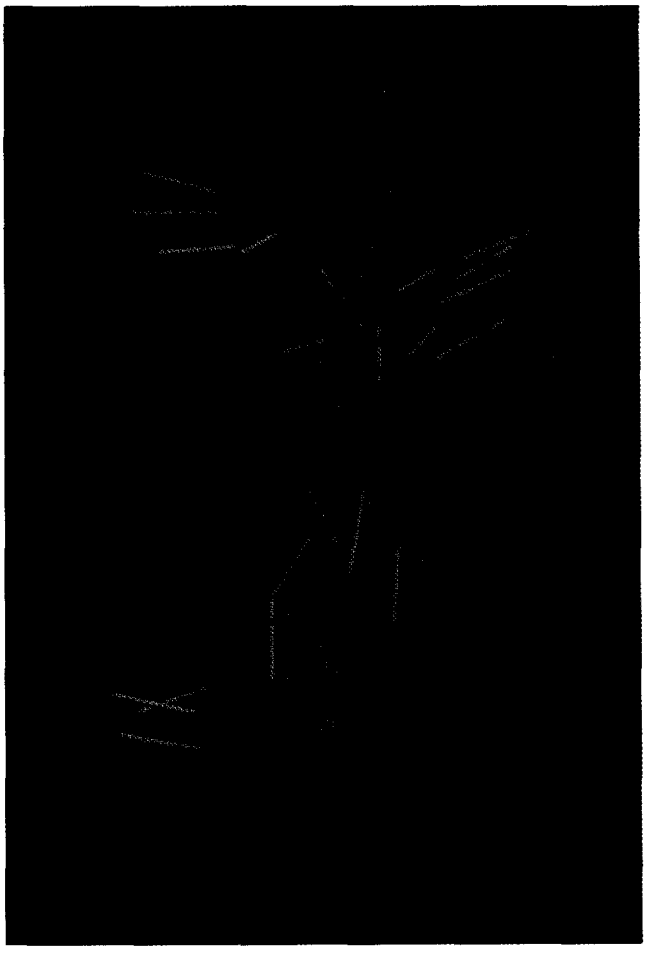

Figure 3 All-biphenyl molecule after 200 ps of MD simulation (orthogonal rod depictions)

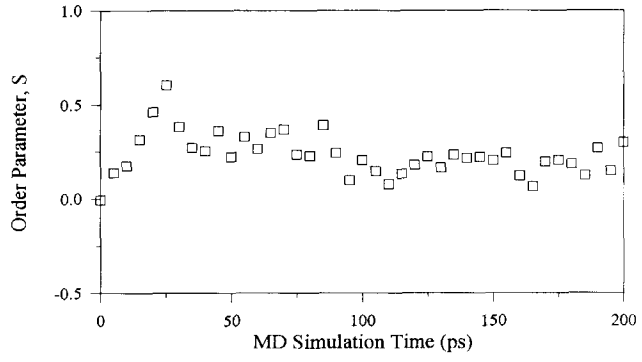

Figure 4 Mesogen order parameter *versus* MD simulation time for all-biphenyl molecule

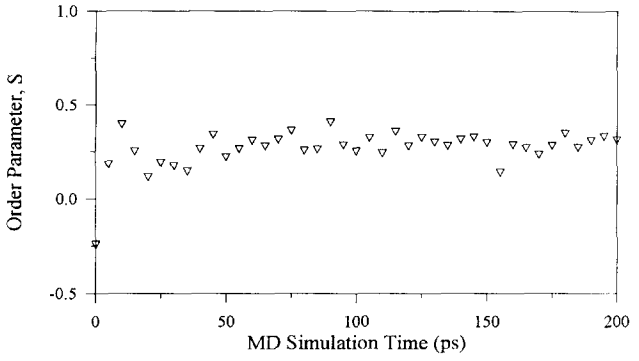

Figure 6 Mesogen order parameter *versus* MD simulation time for all-cholesterol molecule

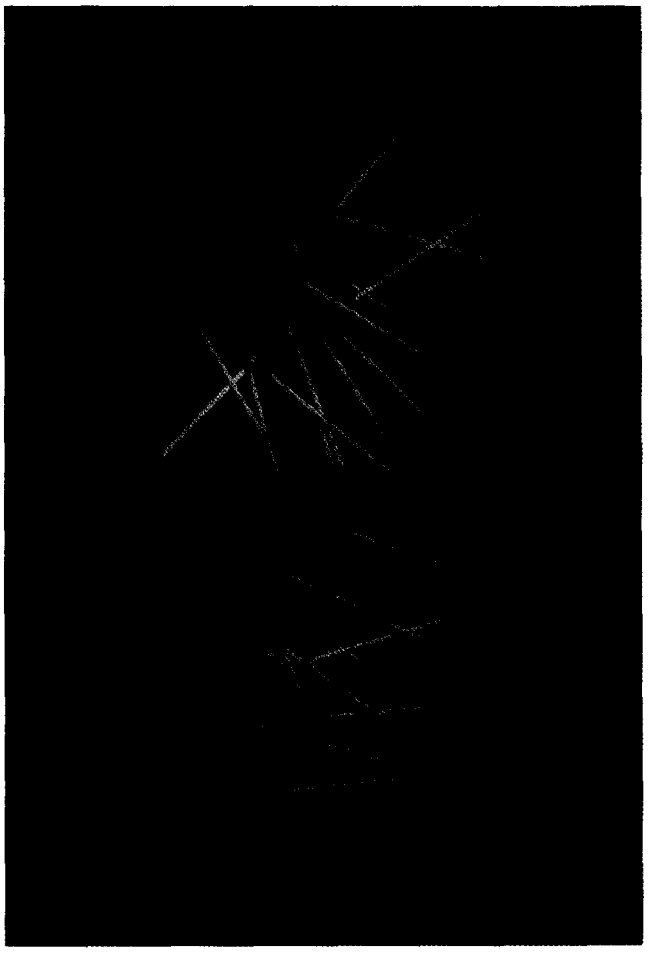

Figure 5 All-cholesterol molecule after 200 ps of MD simulation (orthogonal rod depictions)

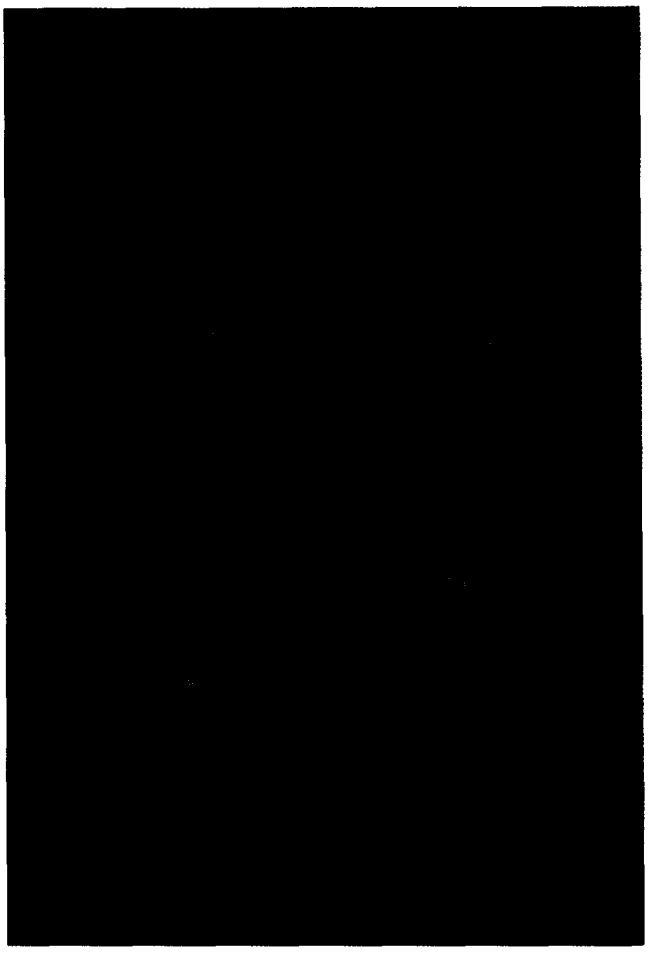

Figure 7 Alternating {B}/{C} molecule after 200 ps of MD simulation (orthogonal rod depictions)

simulation, the order parameter went as high as 0.61. However, after about 100 ps, this value had fallen considerably, and between 150 and 200 ps the order parameter ranged between 0.06 and 0.30 with an average of 0.19, indicating a low level of overall order (see *Figure 4*).

All-cholesterol molecule

The all-cholesterol molecule also developed stable groups of mesogens. *Figure 5* shows orthogonal rod depictions of this molecule after 200 ps of MD. Here, most of the mesogens drew together in a large cluster on one side of the siloxane backbone. The order parameter for the cholesterol was higher than the order parameter for the all-biphenyl molecule. As shown in *Figure 6*, the order parameter varied between 0.15 and 0.35, with an average of 0.29, between 150 and 200 ps. This value indicates a moderate level of overall order for the cholesterol, which was fairly stable over the time range considered.

Alternating {B}/{C} molecule

In the alternating {B}/{C} molecule, the {B} and {C} mesogens formed stable mixed mesogen clusters as well as a few like-mesogen pairs. *Figure 7* shows orthogonal rod depictions of this molecule after 200 ps of MD. As in

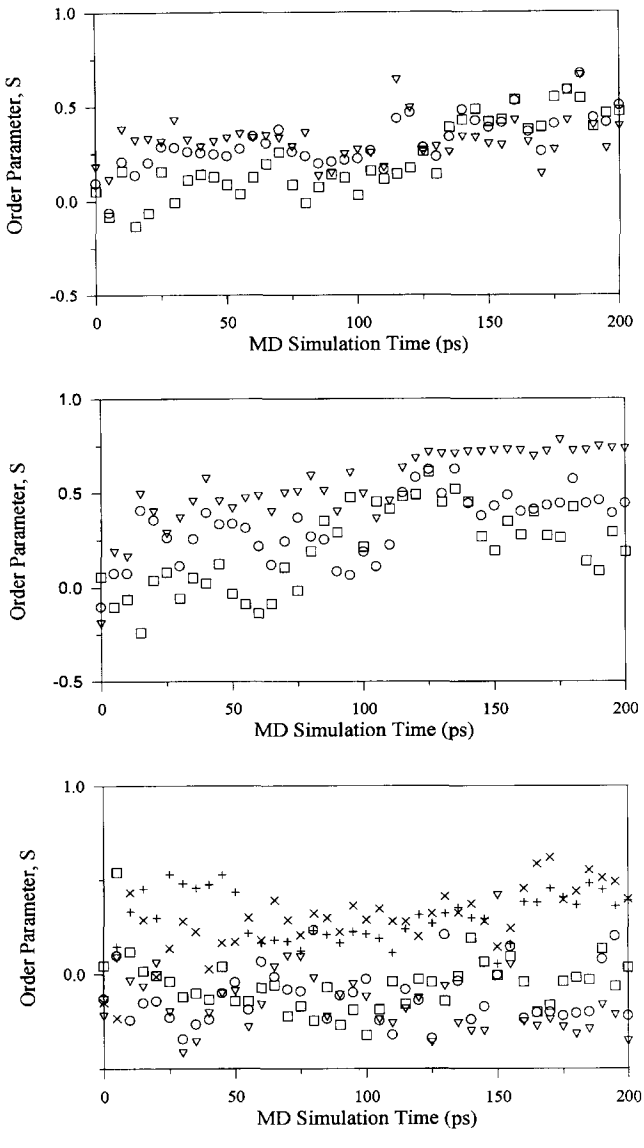

Figure 8 Mesogen order parameter *versus* MD simulation time for mixed mesogen molecules: (a) alternating {B}/{C}, (b) {B}–{C} diblock, and (c) {C}–{B}–{C} triblock. (□) biphenyl only, (▽) cholesterol only, (○) biphenyl and cholesterol, (+) first cholesterol block in {C}–{B}–{C} triblock, and (×) second cholesterol block in {C}–{B}–{C} triblock

the all-cholesterol molecule, a majority of the mesogens formed a large cluster. *Figure 8a* shows the order parameter data *versus* MD simulation time for this molecule. Between 150 and 200 ps, the order parameter for biphenyl ranged between 0.38 and 0.59 and averaged 0.47. The order parameter for cholesterol ranged between 0.15 and 0.67 with an average of 0.36 over the interval 150 to 200 ps. The levels of order for both biphenyl and cholesterol in this molecule are slightly higher than in the single mesogen type molecules, with biphenyl showing a dramatic increase.

{B}–{C} diblock molecule

Stable alignment of both biphenyl and cholesterol mesogens was also observed in the {B}–{C} diblock molecule. *Figure 9* shows orthogonal rod depictions of this molecule after 200 ps MD. It is interesting to note that the biphenyl and cholesterol remained fairly

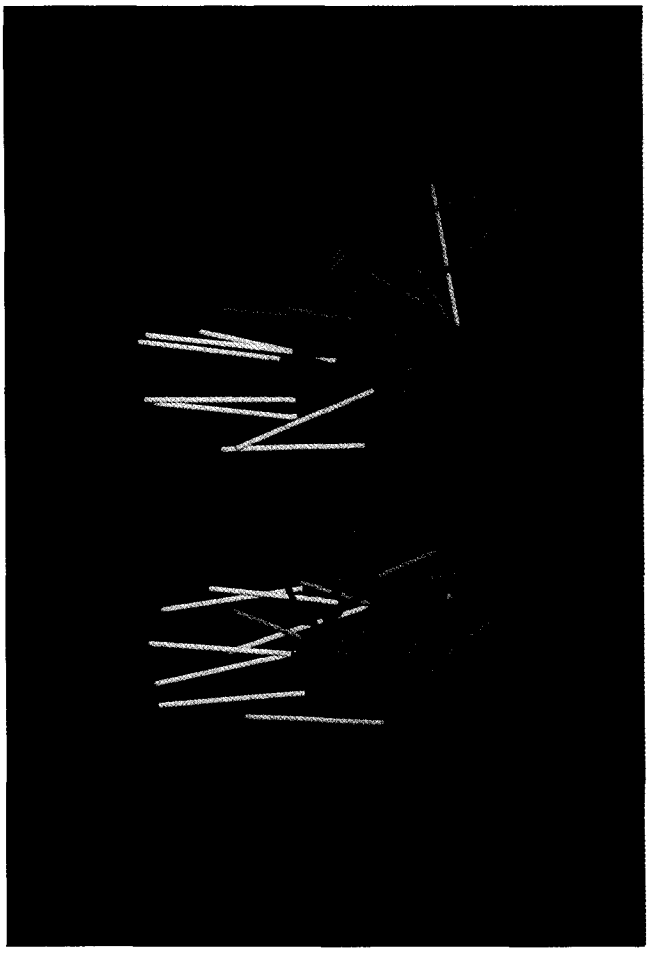

Figure 9 {B}–{C} diblock molecule after 200 ps of MD simulation (orthogonal rod depictions)

separate in this molecule, forming two distinct regions. The order parameter *versus* MD simulation time for the {B}–{C} diblock is shown in *Figure 8b*. Between 150 and 200 ps, the order parameter for the biphenyl fluctuated between 0.09 and 0.42 with an average of 0.26. This indicates a moderate level of order for biphenyl in this molecule, slightly higher than in the all-biphenyl molecule. All but one of the cholesterol mesogens were in a single highly oriented cluster. For the time interval from 150 to 200 ps, the order parameter for cholesterol ranged from 0.70 to 0.79 with an average of 0.74. This higher level of order was very stable over the time period considered.

{C}–{B}–{C} triblock molecule

Alignment of {B} and {C} was seen in the {C}–{B}–{C} triblock as well. *Figure 10* shows a rod depiction of this molecule after 200 ps of dynamics. *Figure 8c* shows the order parameter for this molecule as a function of MD simulation time. Between 150 and 200 ps, the order parameter for the biphenyl fluctuated from −0.20 to 0.13 with an average of −0.03. The order parameter indicates no long range order for the biphenyl, even though stable aligned pairs were present. In this molecule, order parameters were calculated for the two cholesterol blocks considered separately as well as together. The order parameter for the first cholesterol block ranged between 0.05 and 0.48 and averaged 0.35 between 150

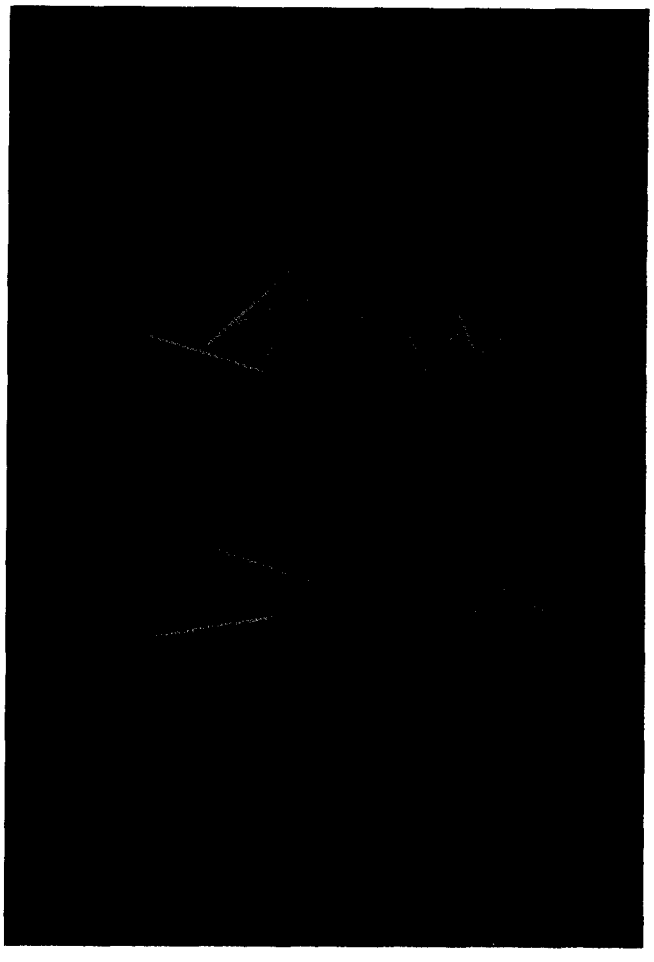

Figure 10 {C}–{B}–{C} triblock molecule after 200 ps of MD simulation (orthogonal rod depictions)

and 200 ps. For the second block, the range was 0.14 to 0.62 and the average was 0.44. These values indicate a moderate level of order for both blocks when considered separately. However, when all of the cholesterol mesogens are considered together, the average is −0.17 with a range from −0.35 to 0.42. This indicates no overall order for the cholesterol.

Order parameter results for biphenyl and cholesterol in each of the five molecules are summarized in *Tables 1* and *2*, respectively. In addition to the order parameter, the associations between all possible pairs of mesogens were monitored throughout the MD simulations. It was observed that {C}–{C} pairs had longer lifetimes than both {B}–{B} and {B}–{C} pairs, with some {C}–{C} associations forming by 25 ps and remaining intact throughout the remainder of the simulation.

Comparison with previous experimental data

Experiments[7] have shown that biphenyl- and cholesterol-substituted linear polysiloxanes exhibit liquid crystalline phases for all mole fractions of biphenyl and cholesterol (i.e. $0 \leq X_C \leq 1$). These phases ranged from nematic for $X_C = 0$, to cholesteric for $X_C = 0.25$ and 0.50, to smectic-A for $X_C = 0.75$ and 1.00 (reference 7). The MD simulation order parameter data presented above show that ordered behaviour was observed in the linear-substituted polysiloxane molecules for $X_C = 0$ (all-biphenyl), $X_C = 0.5$ ({B}–{C} diblock and alternating {B}/{C}), $X_C = 0.625$ ({C}–{B}–{C} triblock), and for $X_C = 1.0$ (all-cholesterol).

The present study calculated order parameters for isolated molecules as a means to compare the alignment behaviour of {B} and {C} mesogens. It is of interest to compare these results to experimental order parameter data. X-ray diffraction experiments on biphenyl-substituted cyclic pentasiloxane aligned in an a.c. electric field found order parameters ranging from 0.3 to 0.55,

Table 1 Comparison of biphenyl order parameter data

	Order parameter				
Molecule	Minimum	Maximum	Range	Average	Level of order
All-biphenyl	0.06	0.30	0.24	0.19	Low
Alternating {B}/{C}	0.38	0.59	0.21	0.47	Moderate
{B}–{C} diblock	0.09	0.42	0.34	0.26	Moderate
{C}–{B}–{C} triblock	−0.20	0.13	0.33	−0.03	None

Table 2 Comparison of cholesterol order parameter data

	Order parameter				
Molecule	Minimum	Maximum	Range	Average	Level of order
All-cholesterol	0.15	0.35	0.21	0.29	Moderate
Alternating {B}/{C}	0.15	0.67	0.52	0.36	Moderate
{B}–{C} diblock	0.70	0.79	0.09	0.74	High
{C}–{B}–{C} triblock					
First block	0.05	0.48	0.43	0.35	Moderate
Second block	0.14	0.62	0.48	0.44	Moderate
All	−0.35	0.42	0.77	−0.17	None

depending on field frequency[11]. MD simulations of this material, using a pre-aligned array of 27 molecules with 135 mesogens, yielded an order parameter of 0.36 (reference 21). Thus, the current result of 0.19 is low, but this is to be expected for the following two reasons. First, no attempt was made to pre-arrange mesogens in an aligned fashion. Instead, alignment was allowed to occur spontaneously. In addition, performing simulations *in vacuo* on such a small system may introduce significant deviations from bulk behaviour.

Main chain behavior

The initial energy minimized conformation of the polysiloxane backbone for each of the molecules was all plus-gauche. During MD simulation, the backbones underwent varying degrees of coiling. The main chain conformation varied slowly with time in each of the substituted molecules. In contrast, a simulation performed on an unsubstituted dimethyl siloxane oligomer showed very wide and rapid fluctuation in chain end-to-end distance over the course of MD simulation. This molecule exhibited dynamic coiling and uncoiling during the simulation, demonstrating (not surprisingly) the wide range of motion possible for the siloxane chain.

An important point to note from these results is that the mesogens displayed the necessary freedom to move rather rapidly to energetically favourable orientations. This is in agreement with experiments[7] that have shown that the highly flexible siloxane backbone, coupled with allyloxybenzoate spacer groups, allows for the formation of liquid crystalline phases in cholesterol- and biphenyl-substituted side chain polymers. The spacer is flexible and reduces steric hindrances to mesogen alignment by spacing the mesogens a distance away from the main chain. This also allows the mesogens to bend around from their point of attachment to the opposite side of the chain.

The speed with which the mesogens reorganized is worth noting. At the outset of this study, it was unclear whether any ordering behaviour would be seen on the time scale of MD simulations. Simulation time on our system is realistically limited to about 1 ns for calculation times on the order of weeks. The ordering of mesogens occurred quite rapidly and, in general, no more than 100 ps of MD was required to see a level of order comparable to that observed at the end of the simulation. However, the amount of time required did vary with molecule type. The all-biphenyl and all-cholesterol molecules took only about 50 ps to rearrange from the starting three-fold helical conformation. The {B}–{C} diblock and alternating {B}/{C} molecules took about 150 ps to find their new arrangements. The {C}–{B}–{C} triblock appeared to achieve a steady level of order by 160 ps.

It is reasonable to question whether the initial arrangement of the mesogens predetermined the associations that would be found later in the simulation. That is, would a pair of mesogens that were initially aligned in one of the branches of the three-fold helix remain so? The alignment of all combinations of mesogen pairs were tracked throughout MD to determine the periods of time that each pair was aligned. It was found that in each of the molecules, at most one mesogen pair present in the initial configuration survived through the simulation. All other pairs were formed during the equilibration and simulation periods of MD. This indicates that the initial arrangement of mesogens was not a controlling factor in the subsequent level of order observed.

DISCUSSION

The presence of small aligned groups of biphenyls in the various molecules demonstrates that the {B}–{B} interaction is energetically favourable. However, this interaction is only able to induce a low level of order in the all-biphenyl molecule because the small groups do not coalesce into larger clusters. On the other hand, larger clusters and a higher degree of alignment are observed in the all-cholesterol molecule. This indicates a favourable {C}–{C} interaction, which is stronger than the {B}–{B} interaction. This is supported by the observation that aligned {C}–{C} pairs have a longer lifetime than aligned {B}–{B} pairs.

When mixtures of {B} and {C} are considered, the arrangement of mesogens along the backbone is as important as the ordering of interaction strengths in determining the level of order. In the alternating {B}/{C} molecule, the presence of both mesogens enhanced the level of order observed for both types, with the level of order for biphenyl more than doubling. This indicates that the {B}–{C} interaction is energetically favourable and that it allows the biphenyl to take advantage of the alignment due to {C}–{C} interactions. In the {B}–{C} diblock molecule, the {B} and {C} remained mostly segregated. The level of order for the biphenyl increased slightly but, more importantly, the level of order for cholesterol better than doubled the all-cholesterol value. A smaller, but noticeable increase in the level of order for cholesterol was observed for the individual blocks in the {C}–{B}–{C} triblock molecule. These observations suggest that small isolated blocks of {C} are able to align to a higher degree than when a larger number are distributed along the backbone. Why should smaller blocks align better than larger ones?

The answer can be found in the {C}–{B}–{C} triblock results. Here, it becomes clear that alignment within the two {C} blocks is partially foiled by the competition between intrablock parallel alignment and interblock antiparallel alignment. The competition between these two low energy arrangements causes the mesogens to split up into small groups aligned either parallel or (roughly) antiparallel. Because the intervening {B} block was very short, the {C} from opposite ends tend to overshoot when trying to align in an antiparallel fashion. The result is a scissor-like arrangement and poor alignment when the two blocks are considered together. A longer {B} block would most likely allow for much better cooperation between the two ends. It is likely that the same type of competition limits the level of orientation in the all-cholesterol molecule.

In all of the molecules, it was observed that the {C}–{C} interaction was dominant, with the biphenyls able to follow along via the weaker {B}–{C} interaction and at best forming small groups via the weaker {B}–{B} interaction. At the same time, it is clear that the arrangement of biphenyl and cholesterol along the backbone may prove critical in engineering the properties of these liquid crystalline polymers.

CONCLUSIONS

The flexible siloxane backbone and allyloxybenzoate spacer group allow biphenyl and cholesterol mesogens in substituted linear polysiloxane great freedom to find energetically favourable arrangements. {B}–{B}, {B}–{C}, and {C}–{C} association and clustering were observed in all of the molecules considered. The clusters of mesogens formed rapidly, usually within 100 ps of MD simulation.

{B}–{B} interactions allowed small clusters to form that were reasonably stable over the time interval simulated. However, these clusters had a range of orientations, and thus led only to a low level of overall alignment of the side chains in the all-biphenyl molecule. {C}–{C} interactions allowed larger stable clusters of cholesterol to form, leading to a moderate level of order in the all-cholesterol molecule. This indicates that the {C}–{C} interaction is stronger than the {B}–{B} interaction.

Mixing biphenyl and cholesterol led to a higher level of order for both types of mesogen in all of the mixed mesogen molecules considered. {B}–{C} interactions, which allow the biphenyl mesogens to associate with the cholesterol, were observed. These were also weaker than the {C}–{C} interaction. While the {C}–{C} interaction was dominant, the arrangement of {B} and {C} along the backbone proved to be very important in determining the level of order observed.

The role of the biphenyl substituent in these systems can be characterized as arising from either (or both) of two effects. The bulkiness of the cholesteric groups and the strength of the {C}–{C} interactions make it difficult for large numbers of {C} mesogens—all tethered to the siloxane backbone—to organize themselves to yield a high order parameter. As exemplified by the triblock molecule, the role of the biphenyl section is to act as a spatial separator, leaving the smaller clusters of {C} more freedom to organize. The second role, seen in the alternating and diblock molecules, can be characterized as that of a 'sticky diluent'. The dilution provides more mobility for the remaining {C} groups, while the stickiness acts to favour larger and somewhat better organized aggregates.

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