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Computer simulations of interactions between liquid crystal molecules and polymer surfaces
II. Alignment of smectic C-forming mesogens

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Computer simulations have been performed to examine the behaviour of the liquid crystalline molecule 4-*n*-heptyl-2-fluoro-phenyl 4-*n*-octyloxybiphenyl-4′-carboxylate (MBF) when in contact with crystalline polymer surfaces. The simulations form part of a study of the alignment interactions that are found in liquid crystal displays. MBF forms several smectic phases including a chiral smectic C* phase when suitably doped. In this paper we examine the way that layers of MBF molecules interact with the structure of the crystalline polymer surface, with the aim of understanding how molecular level interactions give rise to macroscopic phenomena such as the cone angle in ferroelectric liquid crystal devices. Molecular dynamics simulations consisting of a fixed crystalline polymer surface in contact with either a single MBF molecule or up to two layers of them (48 molecules) have been performed. A variety of simple polymer surfaces have been examined and the simulations show that the cone angle is highly dependent on the geometry of both the liquid crystal molecule and the polymer substrate. For molecules of MBF on polyethylene substrates, a cone angle of 20° is predicted, in line with experimental findings.

1. Introduction

The performance of any liquid crystal display is determined by a competition between an external electric field and the aligning influences of the liquid crystal cell surfaces. While the interactions of bulk liquid crystals with external fields are well understood, the behaviour at interfaces is still a subject of debate, and there is much remaining to be learnt in this area. As displays increase in size and complexity, control of the liquid crystal alignment becomes more critical, and it becomes increasingly important to develop an understanding of the mechanisms responsible for orientation of the liquid crystal molecules. In a previous paper [1] we have examined the influence of several crystalline polymer surfaces on the preferred orientations of liquid crystal molecules in nematic and smectic A phases. The present paper focuses attention on the more complex smectic C class of materials which, in chiral form, provide the basis for ferroelectric displays.

Although there are many ways of inducing orientation in a liquid crystal device, perhaps the commonest method is to make use of a polymeric alignment layer which has been prepared by rubbing. The rubbing process is generally thought to operate by one of two possible mechanisms. Orientation is either caused by the formation of grooves [2, 3] or through orientation of the surface layer of the polymer [4, 5]. Recent evidence suggests that the latter mechanism is of most importance in real displays [5–8]. In nematic devices, the rubbing direction coincides with the orientation direction. However, in ferroelectric devices, the molecules prefer to align at some angle to either side of the rubbing direction (see figure 1).

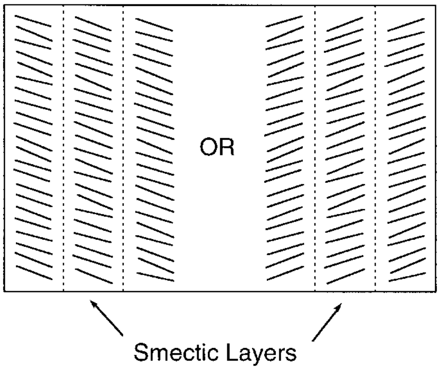

Figure 1. Plan view of a ferroelectric smectic C* cell, looking down on one of the aligning surfaces, which is in the plane of the paper. The two possible tilt orientations are shown: these correspond to the lateral dipoles of the molecules being directed either into or out from the page. The rubbing direction is horizontal.

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These two orientations are related to the cone angle of the cell (see figure 2), which in turn determines the maximum contrast available from the device. The exact relationship is complex and will be discussed further below.

There is an increasing interest in using computer simulation to understand the organization of liquid crystal molecules at interfaces. For example, several groups have reported simulations of ordering phenomena in liquid crystal phases in contact with different types of walls [9–15]. Several simulations have also been presented showing similar phenomena at free liquid crystal surfaces [16–18]. In general these studies have made use of rather simple models, based on the Gay–Berne potential [19], and *ad hoc* representations of the wall. Nevertheless, they are extremely valuable in demonstrating the range of influence of the interface within the bulk liquid crystal phase.

There are currently rather fewer published atomistic simulations of liquid crystal molecules at interfaces, and the nature of atomistic simulations means that generally very small systems have been studied, consisting of, at most, a few tens of molecules. Cleaver *et al.* [20, 21] have considered the interaction between 4-*n*-octyl-4′-cyanobiphenyl (8CB) and a graphite substrate, using molecular mechanics and dynamics, and were able to observe registration between the 8CB molecules and the substrate consistent with scanning tunnelling microscopy results. Yoneya and Iwakabe [22] have reported evidence of alignment in simulations of the same system, and, in addition, have studied 8CB molecules in contact with close packed layers of polyamide and polyimide molecules [23, 24]. The latter simulations demonstrated a preference for the 8CB molecules to align parallel to the polymer chain axis. This finding was supported by our own study of 8CB molecules in contact with several different crystalline polymer surfaces [1].

In this paper, we examine the behaviour of several model systems involving a smectic C-forming mesogen using molecular dynamics simulations. A variety of polymer surfaces are considered, with the aim of comparing predicted liquid crystal alignment directions with experimental cone angles. It is hoped that an understanding of the molecular level interactions between the liquid crystal molecules and the polymer substrates will lead directly to an understanding of the optical contrast observed in real ferroelectric displays.

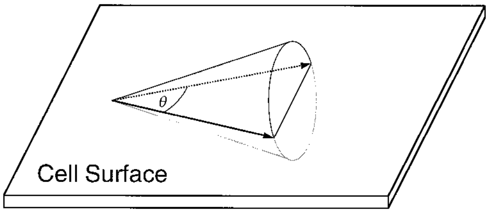


Figure 2. A representation showing the relation between the two director orientations, represented by arrows, and the cone angle θ in a ferroelectric smectic C* phase confined by an aligning surface. The bookshelf geometry is assumed. The rubbing direction is horizontal.

2. Methods and models

2.1. *Molecules and substrates considered*

All of the simulations described in this paper were performed using the liquid crystal molecule 4-*n*-heptyl-2-fluorophenyl 4-*n*-octyloxybiphenyl-4′-carboxylate (MBF) (see figure 3), which forms smectic A, C and I phases and, in particular, forms a smectic C* phase when suitably doped. The polymer surfaces considered were polyethylene (PE), polypropylene (PP), poly(vinyl alcohol) (PVA) and nylon 6. These surfaces were chosen primarily for their simplicity and because optical cone angle measurements have been performed for all of them [25]. PP was included in the set of polymers considered as an example of a material which does not normally induce a planar liquid crystal alignment [25]. Only crystalline polymer surfaces were considered, since it is known that amorphous polymers are poor at aligning ferroelectric materials [25–27]. The surface structures were obtained from published crystallographic data [28–31]. A summary of the surfaces considered is given in table 1. These crystal faces were considered to be the most likely to occur in rubbed polymer systems for reasons which have been summarized elsewhere [1].

2.2. *Simulation methods*

Molecular dynamics simulations were performed using the Cerius^2 molecular modelling package [32] and the Dreiding2 force-field [33]. All CH, CH_2 and CH_3 groups were replaced with united atoms in order to reduce the

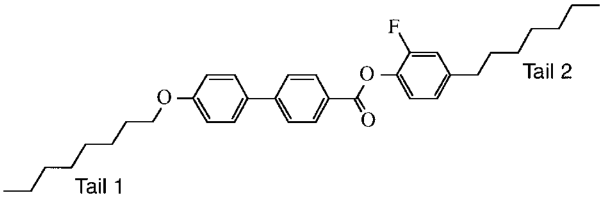


Figure 3. The MBF molecule. The two alkyl tails are labelled.

Table 1. A summary of the polymers and crystal faces used as aligning surfaces in the molecular dynamics simulations.

Material	Crystal face
PE	(1 1 0), (1 0 0)
Nylon 6	(0 1 0)
PVA	(1 0 0)
PP	(1 1 0)

computer time needed. The Dreiding2 force-field was selected for its simplicity and on the grounds that we were primarily interested in the general behaviour of liquid crystal molecules on polymer surfaces, rather than subtle details. Indeed, the use of united atoms limits the extent of realism that is possible in such simulations, making it inappropriate to use more complicated force-fields. Another consequence of the use of united atoms was that the biphenyl unit in the liquid crystal backbone could become planar during the simulations. Therefore, it was necessary to modify the biphenyl torsional potential, as described previously [1], in order to compensate for this effect. Electrostatic interactions were not included in the simulations, except where explicitly stated. When they were included, partial charges were determined by use of the MOPAC molecular orbital package [34] or the Gasteiger electronegativity method [35]. The charges obtained by both methods were very similar.

Simulations consisted of either a single liquid crystal molecule or up to two monolayers of molecules, in contact with one of the polymer surfaces. The term 'monolayer' is used here in a general sense to refer to a finite patch of molecules, a single molecule thick. In order to reduce computational expense, the atoms in the polymer surface were not permitted to move during the simulation. For the single molecule simulations, 16 independent starting orientations were used, to ensure that phase space was adequately explored. Each simulation was equilibrated for 100 ps, and the total data collection time was 4 ns. However, for the monolayer simulations, the initial configurations of the liquid crystal molecules were determined from the preferred orientations given by the single molecule simulations, so that the liquid crystal molecules were initially already close to their expected equilibrium orientations. The monolayer simulations were also equilibrated for 100 ps, and data were collected for 1 ns. Previous studies with other liquid crystal molecules have indicated that 100 ps should be sufficient time for the liquid crystal molecules to reorient through angles of up to 45° and thus lose any memory of their initial orientation [1].

The overall durations of all of the simulations were selected to ensure reproducibility of the orientation distribution functions (ODFs). This was generally achieved, to the extent that ODFs determined from independent simulations were qualitatively similar, but had statistical variations in the heights of the observed peaks. All simulations were performed at 300 K using a 2 fs time step and the microcanonical ensemble was used for sampling. The simulations were performed on several Unix work stations and a Silicon Graphics Origin 200 server. The molecular images shown in the figures were created from the co-ordinates generated by Cerius^2, using the PovChem ray-tracing program [36].

In addition to the molecular dynamics simulations, an energy minimization study was performed to find the energetically most favourable orientation of the MBF molecule on each surface.

2.3. *Analysis of results*

Orientational distribution functions (ODFs) were calculated from the molecular dynamics trajectories for the liquid crystal core and for each of the tails. The orientations were determined from the principal axes of the moment of inertia tensor for each fragment. The ODFs are shown using polar coordinates for clarity. The square root of the frequency of each orientation is plotted versus the angle, in order that the areas of each plot may be correctly normalized. However, peak positions and widths were measured from simple rectangular plots of frequency versus angle which are not shown here, except for the bilayer simulations, where their inclusion improves the clarity of the argument. In addition, lateral pair-wise correlation functions were calculated for the positions of the molecules in the monolayer simulations, projected on to a direction perpendicular to the polymer chain axis.

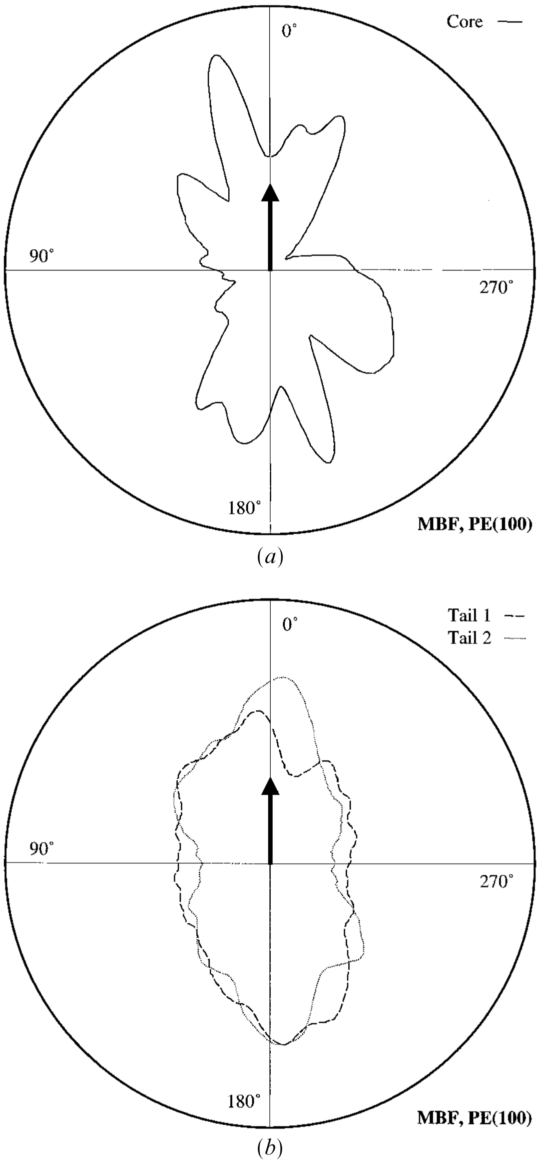
Orientational order parameters, $\langle P_2 \rangle$, $\langle P_4 \rangle$ and $\langle P_6 \rangle$, were calculated directly from the ODFs, using the method described by Windle [37], which enables the figures computed from 2-dimensional monolayers to be compared with bulk experimental values. All ODFs, orientation parameters and correlation functions presented here were averaged over the whole period of each simulation. No evidence was found for time-dependence of any of these quantities once the models had equilibrated, the only variations seen being statistical in nature.

3. Results

As detailed above, the simulations consisted of two types: simulations of isolated molecules and simulations of monolayers of liquid crystal molecules on polymer surfaces. The results for isolated MBF molecules on PE substrates are considered first. These will be contrasted with the results from monolayer simulations on the same surfaces. Finally, the influence of different polymer surfaces will be considered.

3.1. *Isolated MBF molecule on PE*

Simulations were performed on the (1 0 0) and (1 1 0) surfaces of PE. Typical ODFs for the MBF cores and alkyl tails are shown in figures 4 and 5, and summarized in table 2. On both the (1 0 0) and (1 1 0) surfaces, the ODFs for the core show a series of distinct peaks at different angles to the polymer chain direction. The tails, on the other hand, remain substantially parallel to the chain axes, although there is considerable variation in the angles adopted: the average widths of the peaks



(*a*)

(*b*)

Figure 4. ODFs for (*a*) the rigid core and (*b*) both tails of an MBF molecule in contact with the (1 0 0) surface of PE; the two tails are identified in figure 3. The direction of the polymer chain axis is indicated by the bold vertical arrow.

for the tails in the ODFs are 60° and 35° for tail 1 and tail 2, respectively, compared with 15° for the core peaks. Preliminary results for MBF molecules on the (1 1 0) surface of PE were also shown in a previous communication [38]. The irregularity in the ODFs is due to a non-uniform sampling of configurational space. This appears to be a result of the MBF molecule having a low mobility on the PE surfaces, which is probably a consequence of the large size of the molecule. In similar simulations of the smaller liquid crystal molecules 5CB and 8CB, the mobilities were found to be considerably greater and the ODFs correspondingly more regular [1].

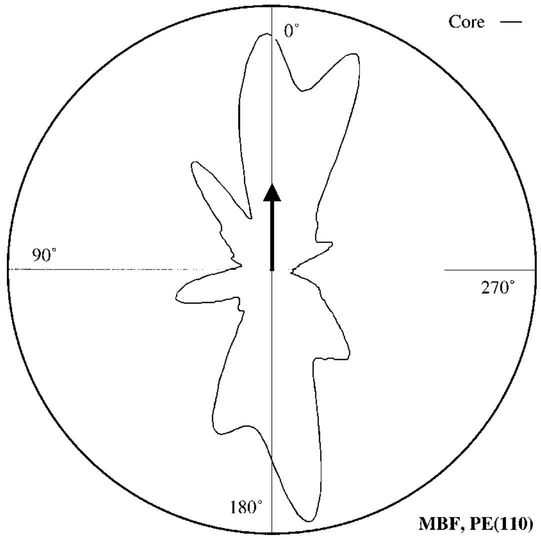


Figure 5. ODF for the rigid core of an MBF molecule in contact with the (1 1 0) surface of PE.

From inspection of the molecular dynamics trajectories, the angles adopted by the rigid molecular cores are found to correspond to the molecule straddling one or more substrate polymer chains; this is illustrated in figure 6. Angles in the range 15° to 30° from the polymer axis correspond to the core straddling a single polymer chain, angles between 30° and 45° correspond to the straddling of two polymer chains and angles greater than 45° to the straddling of three or more polymer chains. Angles less than 15° correspond to the core lying entirely within a single molecular corrugation on the polymer surface.

The wide range of preferred orientations of the core raises the question of whether the alignment is driven by a preference for the alkyl tails to lie parallel to the polymer chains in the substrate, or by the energetic preferences of the core itself. In order to attempt to answer this question, simulations were performed on both surfaces of PE using an isolated MBF core, i.e. an MBF molecule with the alkyl tails removed. The ODFs for this system are shown in figure 7 and summarized in table 2. The similarities with the ODFs in figures 4 and 5 are pronounced, and it is clear that, even without the presence of alkyl tails, the core is adopting configurations which straddle one, two or three polymer chains. However, the anisotropy in the ODFs from the isolated cores is slightly less pronounced than is observed with the MBF molecules, suggesting that the alkyl tails may play a role in stabilizing the straddled configurations.

Further evidence for the preferential alignment of the core was provided by an energy minimization study. An MBF molecule was placed on the (1 0 0) surface of PE, and its long axis was rotated in 5° steps about the substrate normal. At each angle, the energy of the system

Table 2. The positions of the peaks in the ODFs for the simulations of isolated MBF molecules in contact with a variety of polymer surfaces. All angles are given in degrees. The accuracy of each peak position is approximately ± 3°, except where stated otherwise. The average peak widths are also shown.

	Angles/°			Average Widths/°		
Surface	Core	Tail 1	Tail 2	Core	Tail 1	Tail 2
PE (1 0 0)	12, 42, 155, 170, 195, 240 ± 10, 335, 347	3, 184, 330	0, 183, 225	15	60	35
PE (1 1 0)	4, 36, 105, 161, 188, 219, 337	0	5, 175	15	60	40
PE (1 0 0) Isolated core	17, 53, 150, 174, 195, 235, 331, 350	—	—	15	—	—
PE (1 1 0) Isolated core	10, 42, 115, 159, 178, 190, 220, 302, 340, 350	—	—	15	—	—
PVA (1 0 0)	13, 47, 152, 175, 230, 333, 350	0, 180	0, 180	10	20	30
Nylon 6 (0 1 0)	10, 43, 155, 167, 190, 222, 334	180	0, 175	15	30	40
PP (1 1 0)	35, 68, 81, 112, 133, 173, 202, 218, 250, 260, 291, 320, 355	111, 315	111, 163, 296, 342	15	45	30

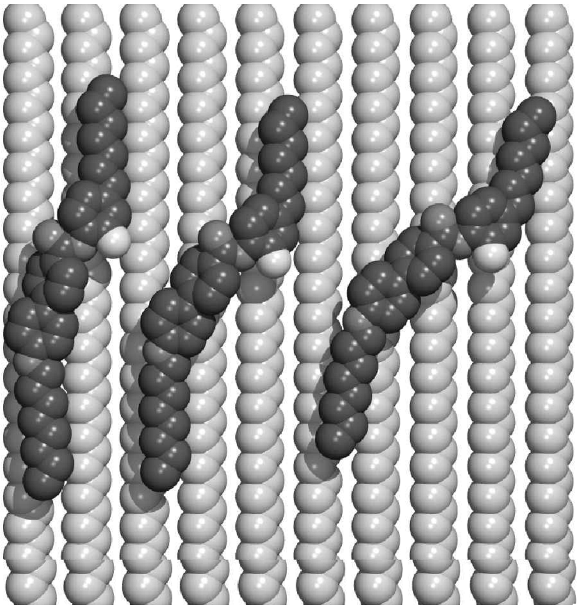


Figure 6. Three configurations of MBF on the (1 0 0) surface of PE; moving from left to right, the molecule straddles one, two or three PE chains, respectively, giving different orientations for the core in each case. It is also possible for the core to lie parallel to the PE chains, but then one of the tails is usually observed to lie at an angle to the polymer chains. Molecular images created using Cerius^2 and rendered using PovChem.

was minimized using a conjugate gradient method. The molecule was then rotated by 180° about its long axis and the process repeated. The result is a map of the local energy minima which are closest to the initial orientation of the molecule (see figure 8). The lowest energy configurations were found to be those with the tails almost or completely parallel to the chains in the substrate, but with the core traversing one or two chains. In the higher energy states found, neither of the tails is parallel. There is a clear correspondence between the lowest energy configurations found in the minimization study and the peaks in the ODFs.

One other factor which may influence the observed alignment is the shape of the molecule. We may define this, in simple terms, as the angle that the rigid core makes with each of the tails. From an energy minimization of an MBF molecule in free space, the preferred angles are found to be 38° between the core and tail 1, and 27° between the core and tail 2. Thus, we might expect that the most stable configuration will be one with the alkyl tails parallel to the polymer chains, and the core aligned in the range 27° to 38°. In fact, as is clear from the molecular dynamics simulations, there is sufficient flexibility in the tails to allow several stable orientations.

The overall picture which emerges from the above simulations is that there are several factors contributing to the observed orientations of the MBF molecules. The natural tendency of the alkyl tails is to lie parallel to the polymer chains, while the core prefers to straddle one or more polymer molecules. The lowest energy conformation of the MBF molecule is fortuitously consistent with these requirements, making the most likely orientations those in which the MBF core straddles one or two polymer molecules. However, as has been shown, at ambient temperatures, configurations in which either zero or three polymer chains are straddled are also possible.

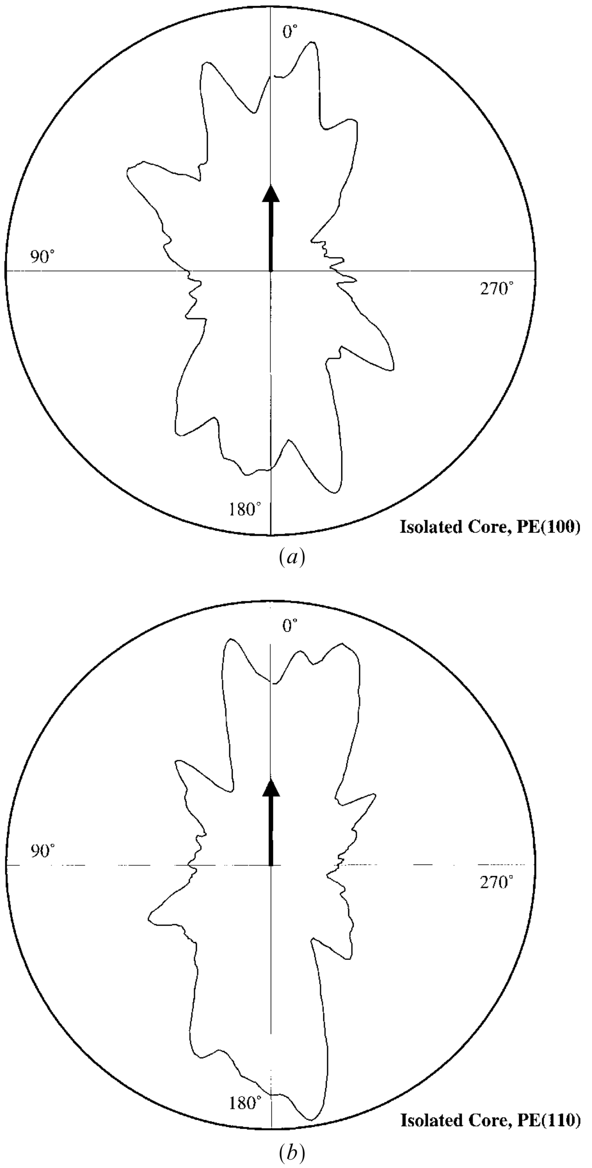


Figure 7. ODFs for the isolated rigid core constructed from an MBF molecule on (*a*) the (1 0 0) and (*b*) the (1 1 0) surface of PE.

In order to confirm that our findings are not influenced by the use of the united atom approximation, additional simulations were performed using explicit hydrogen atoms. The ODFs obtained from these simulations were qualitatively similar to those obtained using united atoms, with only minor differences observed in the positions and heights of peaks observed. Thus, it would appear that the use of the united atom approximation is valid in the present context.

3.2. *Monolayers of MBF on PE*

The single molecule simulations described above are intriguing, because they suggest the possibility that the MBF molecule may show a natural tendency to align at a non-zero angle to the underlying polymer chains, which, in turn, may suggest a mechanism for the occurrence of surface stabilization in ferroelectric displays. However, some caution is needed at this stage, since previous experience with simulations of 8CB molecules suggests that the behaviour of an isolated molecule may be quite different from that of a close packed ensemble of molecules [1]. For this reason, a series of simulations of monolayers of MBF molecules was performed on the (1 0 0) surface of PE, as described below.

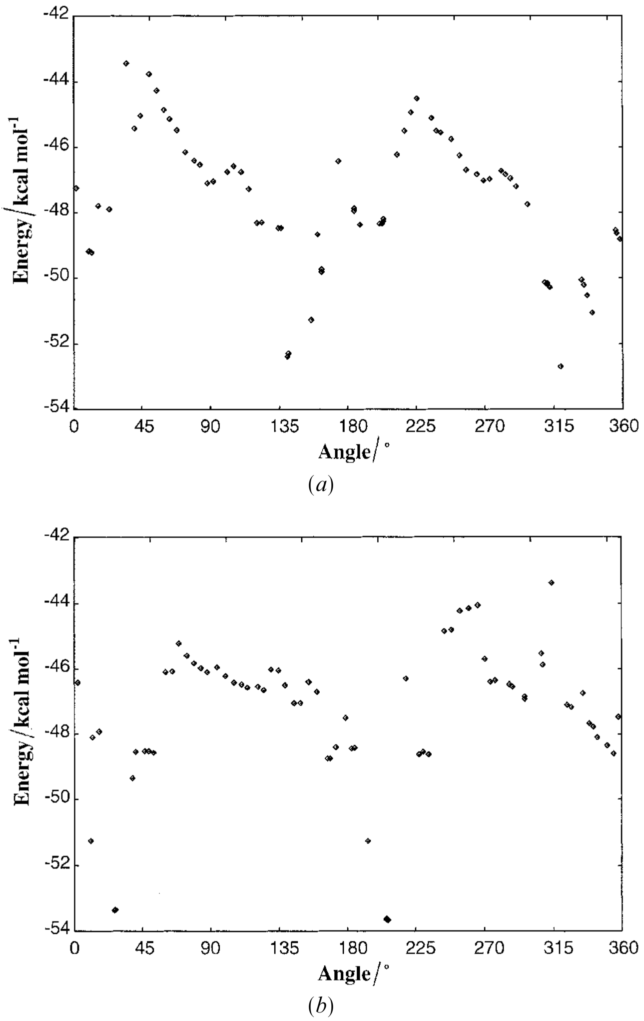


Figure 8. (*a*) The energy of an MBF molecule on the (1 0 0) surface of PE after minimization, plotted against the final orientation of the molecular core, for a sequence of minimizations with different starting configurations. (*b*) A similar plot to (*a*) with the MBF molecule rotated by 180° about its long axis; the points are clustered in the vicinity of each energy minimum.

Simulations were performed with starting configurations consisting of two banks of eight molecules, arranged as shown in figure 9. Several starting configurations were

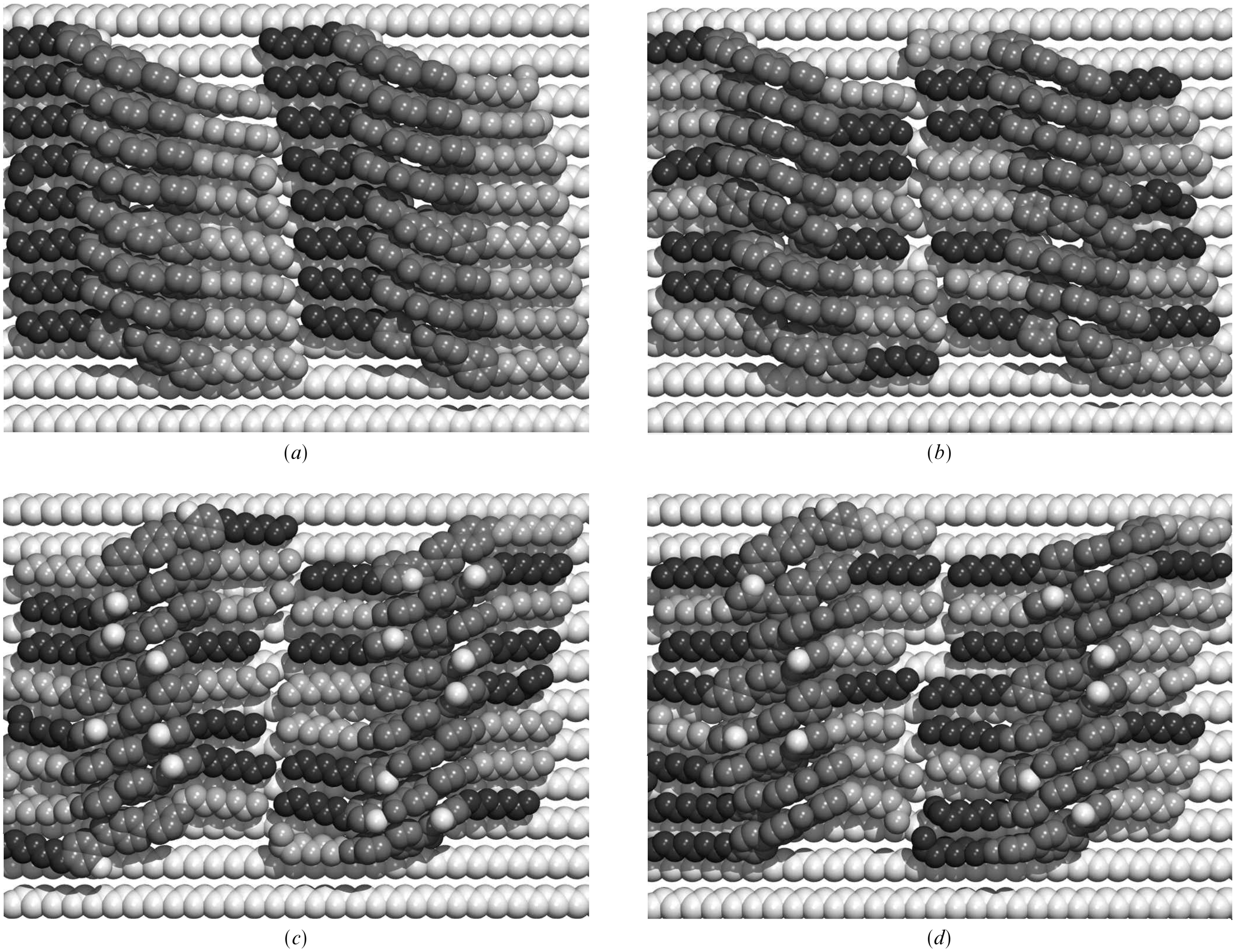
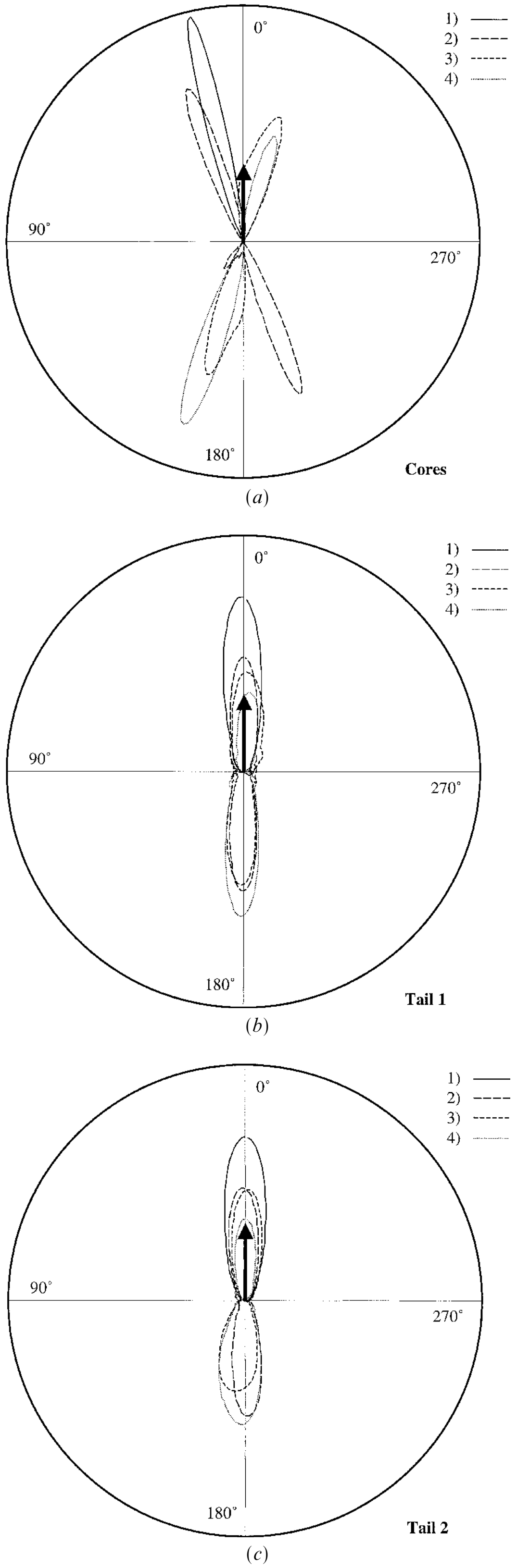

(*a*) (*b*) (*c*) (*d*)

Figure 9. The four starting configurations employed in the single monolayer simulations of MBF molecules on the (1 0 0) surface of PE. (*a*) Simulation 1: uniform configuration, all fluorine atoms pointing down. (*b*) Simulation 2: random configuration, all fluorines down. (*c*) Simulation 3: random configuration, all fluorines up. (*d*) Simulation 4: random configuration, random fluorine orientations. The tails and fluorine atoms are distinguished by different shades of grey. Molecular images created using Cerius^2 and rendered using PovChem.

employed, differing in the orientations of the MBF molecules. In the first simulation, the MBF molecules were arranged in a uniform configuration with all of the tails 1 adjacent to each other, and all of the substituent fluorine atoms directed down towards the substrate. In the second simulation, the fluorine atoms were also facing the substrate, but the molecules were randomized with respect to rotations about the surface normal, so that tails 1 and 2 could be side by side in adjacent molecules. The third simulation was identical to the second, except that the molecules were rotated by 180° about their long axes, so that the fluorine atoms were oriented away from the polymer surface. The fourth was derived from the third, with the fluorine atoms pointing randomly towards or away from the surface. In all of the starting configurations, the tails of each molecule were rotated so that they were parallel to the polymer chains, and the total energy of the system was then minimized before any molecular dynamics were attempted.

For all of the simulations, the ODFs were calculated for the cores and tails and are shown in figure 10. The lateral pair-wise translational correlation function was also calculated and is shown in figure 11 (*a*). The ODFs show very clearly defined peaks compared with the single molecule simulations. In each simulation, the cores and tails each showed a single preferred alignment direction. In all of the simulations, the tails showed a marked preference for aligning parallel to the polymer chain axis. The cores, on the other hand, preferred to align at up to 20° to the polymer axis, with the precise

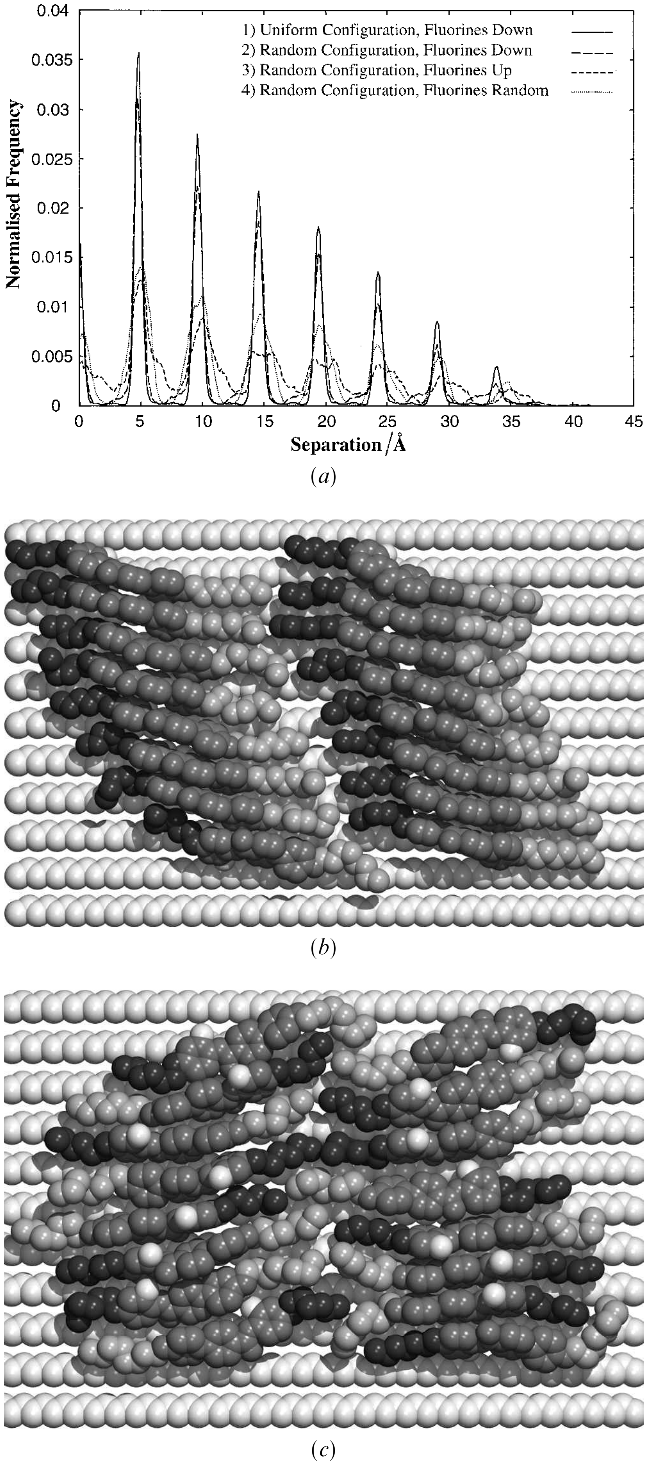


(*a*)

(*b*)

(*c*)

Figure 10. The ODFs for the cores and tails obtained from each of the simulations of monolayers of MBF shown in figure 9: (*a*) MBF cores; (*b*) tail 1; (*c*) tail 2.



(*a*)

(*b*)

(*c*)

Figure 11. (*a*) The pair-wise translational distribution function, calculated from the four MBF monolayer simulations shown in figure 9. (*b*) Snapshot taken from simulation 1 and (*c*) snapshot taken from simulation 4, after 800 ps, showing an apparent difference in positional ordering. Molecular images created using Cerius^2 and rendered using PovChem.

angle depending on the starting configuration. The core peak width was narrowest for simulation 1, which corresponded to the most ordered starting configuration, suggesting that the order persists throughout the simulation. This is confirmed by a snapshot taken after 800 ps, figure 11 (*b*), and by the lateral positional correlation function, which shows a series of narrow peaks with a spacing of 4.9 Å, corresponding to the chain spacing in the (1 0 0) surface. In fact, the peaks in the correlation function become increasingly diffuse as the level of order in the starting configurations decreases, with the exception that simulation 4 is slightly more ordered than simulation 3. The spreading of the peaks is an indication that the molecules are less confined in their translational motion on the surface, as can be seen by comparing figure 11 (*c*), which is a snapshot from simulation 4 taken after 800 ps, with figure 11 (*b*), which was taken after a similar length of time from simulation 1. The peak widths are also an indication of the closeness of packing of the molecules, which necessarily deteriorates as the regularity of the configuration decreases. Furthermore, the differences between the correlation functions for simulations 2 and 3, and between simulations 3 and 4, suggests that the orientation of the fluorine atoms is important in obtaining a close contact between the MBF molecules and the polymer substrate.

3.3. *Bilayers of MBF on PE*

The monolayer simulations demonstrate that, as was previously found for 8CB [1], it is possible for the adsorbed molecules to display an almost crystalline level of order. It is of interest, therefore, to examine the influence that the first adsorbed layer has on the structure of the second and subsequent adsorbed layers, in order to attempt to understand the interaction between the polymer surface and the bulk liquid crystal.

A simulation was performed of a bilayer of MBF molecules on the (1 0 0) surface of PE. Each layer consisted of three banks of eight molecules, making a total of 48 molecules in the simulation. The MBF molecules were arranged in a uniform configuration, similar to the first monolayer simulation described above. A side view of the starting configuration is shown in figure 12, together with a snapshot of the configuration after 800 ps. Simulations were performed with and without electrostatic interactions. However, identical results were obtained in both cases.

The ODFs for the MBF tails and cores were calculated separately for each monolayer, and are shown in figure 13. Rectangular plots are shown in order to emphasize the differences in peak widths. The corresponding lateral translational correlation functions are shown in figure 14. The ODFs for the first monolayer, i.e. the monolayer in direct contact with the PE surface, are consistent with the results from the first monolayer simulation above. The tails align parallel to the polymer chains, and the cores are inclined at 20°. The peak width for the core is *c.* 10°, while the widths for the tails are *c.* 30°. However, the second monolayer shows a marked difference. All of the peak widths have broadened, suggesting that the second monolayer possesses considerably less orientational order than the first. In fact, the orientational order parameter, $\langle P_2 \rangle$, calculated from the core distributions, only decreases from 0.98 for the first monolayer to 0.95 for the second (see table 3). However, the differences are more marked in the higher order terms, with there being a clear decrease in orientational order from the first to the second layer. In addition, the centres of the peaks in the ODFs have shifted. The preferred orientation of the cores in the second monolayer is at 10°, while tails 1 and 2 have moved to 5° and 15°, respectively. The projected shape of the molecules in the second layer is thus straighter than in the first layer as well as being less ordered, and the tails are no longer parallel to the chain direction.

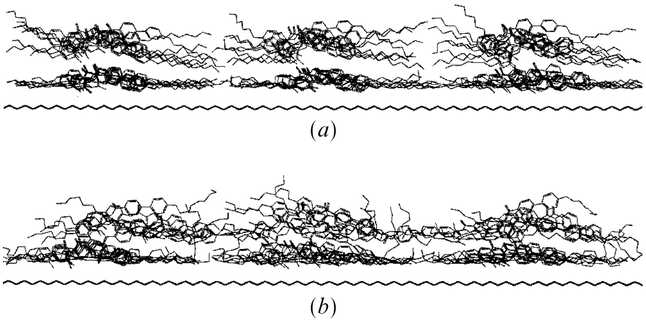

(*a*)
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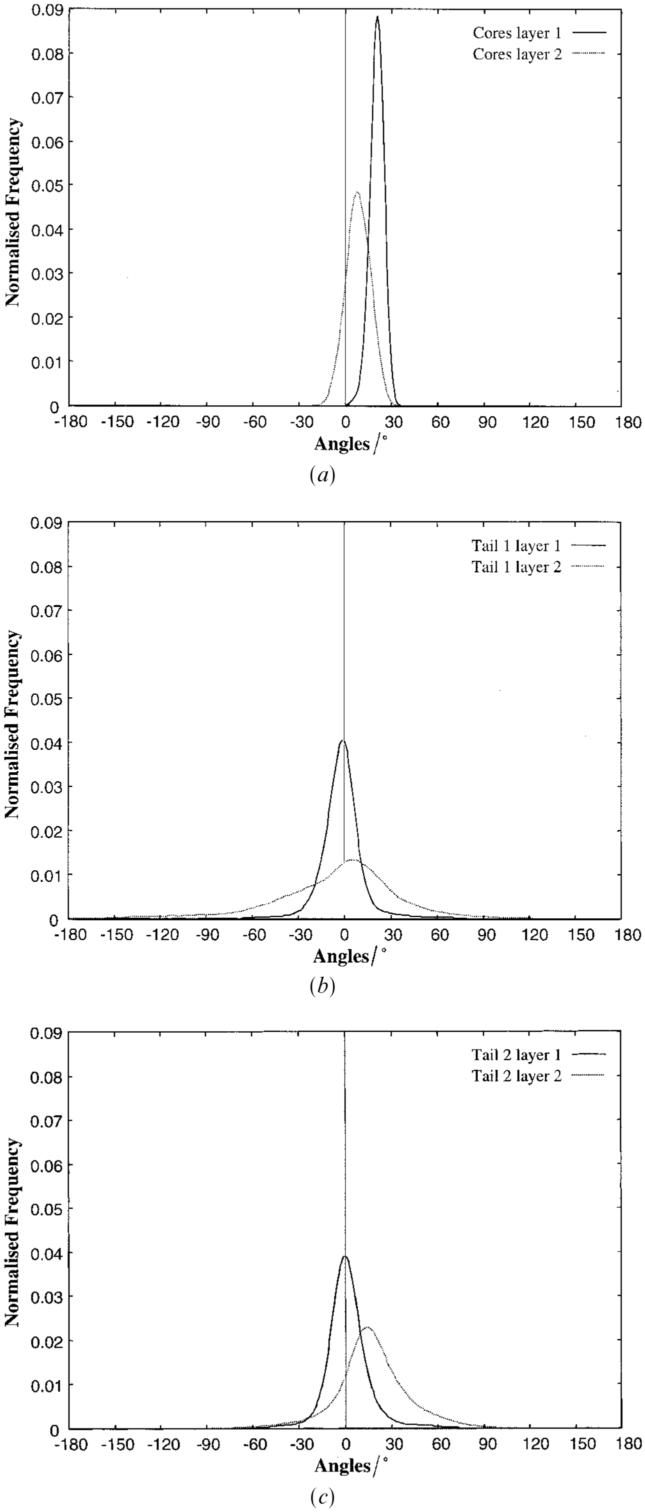
Figure 12. (*a*) Side view of the starting configuration of the bilayer simulation of MBF on the (1 0 0) surface of PE; there are 48 molecules arranged in two layers which can be seen clearly. (*b*) Similar view after 800 ps of simulation time. Molecular images created using Cerius^2.

The translational correlation function (figure 14) shows an even more pronounced difference between the two layers. The first layer shows a series of regularly spaced peaks, with the distribution dropping to zero in between. Thus the molecules show a strong correlation with the PE chains in the substrate and show little tendency to move sideways across the chains. In fact, the molecules are almost locked into place, as in monolayer simulation 1. The second layer is very different

Table 3. The orientational order parameters, $\langle P_2 \rangle$, $\langle P_4 \rangle$ and $\langle P_6 \rangle$ calculated from the ODFs for the 48 MBF molecule bilayer simulation.

Layer No.	$\langle P_2 \rangle$	$\langle P_4 \rangle$	$\langle P_6 \rangle$
1	0.98	0.95	0.89
2	0.95	0.84	0.70



(*a*)

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Figure 13. The ODFs for the MBF molecules in each layer of the bilayer simulation: (*a*) MBF cores; (*b*) tail 1; (*c*) tail 2.

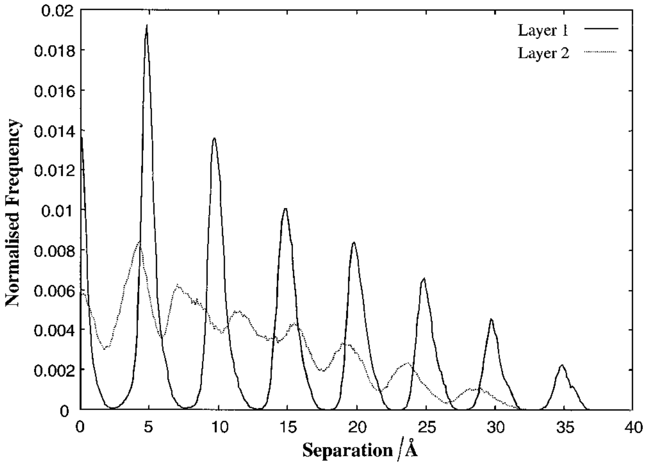


Figure 14. Translational correlation function normal to the chain axis for the molecules in the first and second layer of the bilayer simulation.

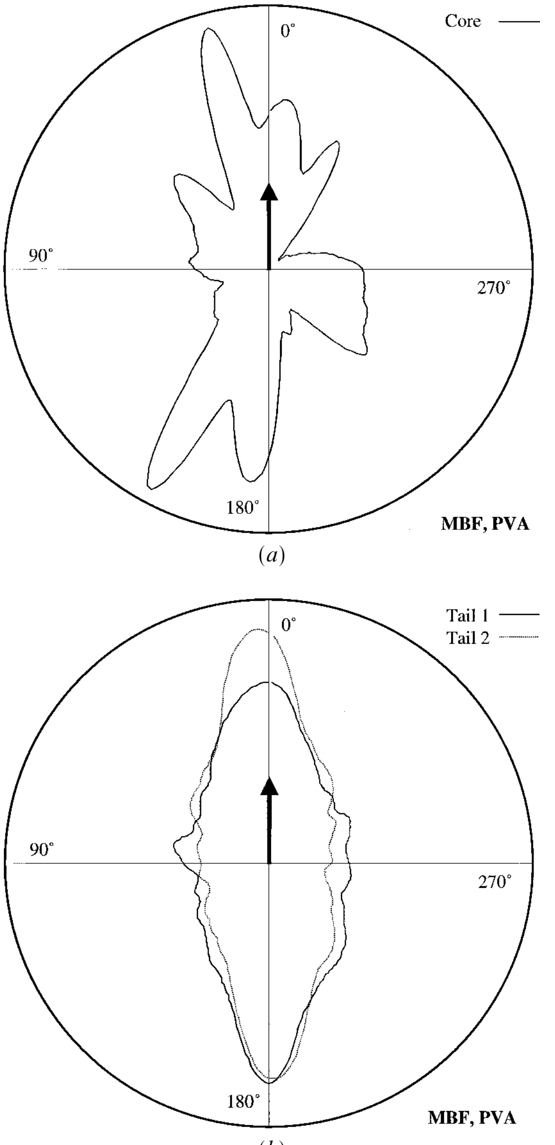
in character. The correlation function no longer has distinctive peaks, but consists of a single broad distribution with a periodic modulation in amplitude. The period of the modulation is slightly less than that of the first layer. The distribution thus indicates that the molecules have a much increased degree of translational freedom and are not locked into place, as compared with the first layer.

It is interesting to note that, although the translational order is quickly lost on going from the first to the second monolayer, much of the orientational order is kept. It would be interesting to consider how this orientational order propagates through a larger number of layers to align the bulk, but that is beyond the scope of the present study.

3.4. *Simulations on other polymer surfaces*

Although PE is a convenient model substrate to use in simulation studies, it is not usually used in practical liquid crystal devices. For this reason, and because we wish to examine whether the behaviour described above is specific to PE surfaces, simulations have been performed of isolated MBF molecules on PVA, Nylon 6 and PP substrates. PP was selected as a surface which was not expected to produce any alignment. The PVA and Nylon 6 simulations were performed with and without electrostatic interactions. However, the results obtained were qualitatively similar in both cases. The main differences appeared in the relative heights rather than the positions of the ODF peaks, and could be attributed to poor sampling rather than any systematic variation.

The ODFs for the tails and core of an isolated MBF molecule on the (1 0 0) surface of PVA are shown in figure 15 and summarized in table 2. As with PE, the cores show a succession of preferred orientations. However, the peaks are narrower for PVA than for PE, suggesting that the molecule is better aligned. The differences are



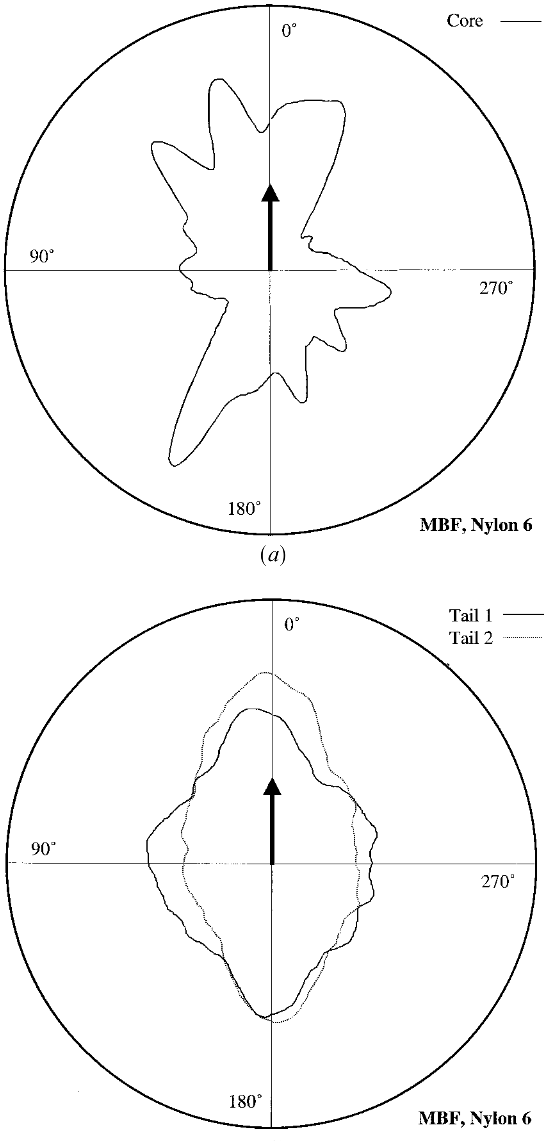
(*a*)

(*b*)

Figure 15. ODFs for (*a*) the core and (*b*) the tails of an isolated MBF molecule on the (1 0 0) surface of PVA.

most marked for the tails, which align parallel to the polymer chains with peak widths of 20° to 30° for PVA compared with 30° to 60° for PE. The difference in alignment between the two surfaces can be understood in terms of the chain spacing and the degree of surface corrugation. Similar effects were observed in simulations of 8CB and 5CB molecules [1]. The molecular corrugations in PVA are wider and deeper than in PE, allowing better registration of the tails with the substrate. The orientations adopted by the core may be determined from simple geometry and, as in the case of PE, correspond to the straddling of one or more polymer chains.

The ODFs for the (0 1 0) surface of Nylon 6 are shown in figure 16. The distributions show the same



(*a*)

(*b*)

Figure 16. ODFs for (*a*) the core and (*b*) the tails of an isolated MBF molecule on the (0 1 0) surface of Nylon 6.

general trends as the PE and PVA surfaces, with the distribution for the core showing a number of peaks at a range of angles, and the tails predominantly parallel to the polymer chain axis. The peak widths of the tails are quite broad, resembling those on PE more closely than those on PVA.

The ODFs for the (1 1 0) surface of PP (figure 17) are quite different from those on the other substrates. The core and tails display a wide range of possible angles, with no single direction dominating. This finding is consistent with the observation that planar alignment of liquid crystals is not found using PP substrates [25]. However, these findings cannot be taken as proof that a homeotropic alignment will occur.

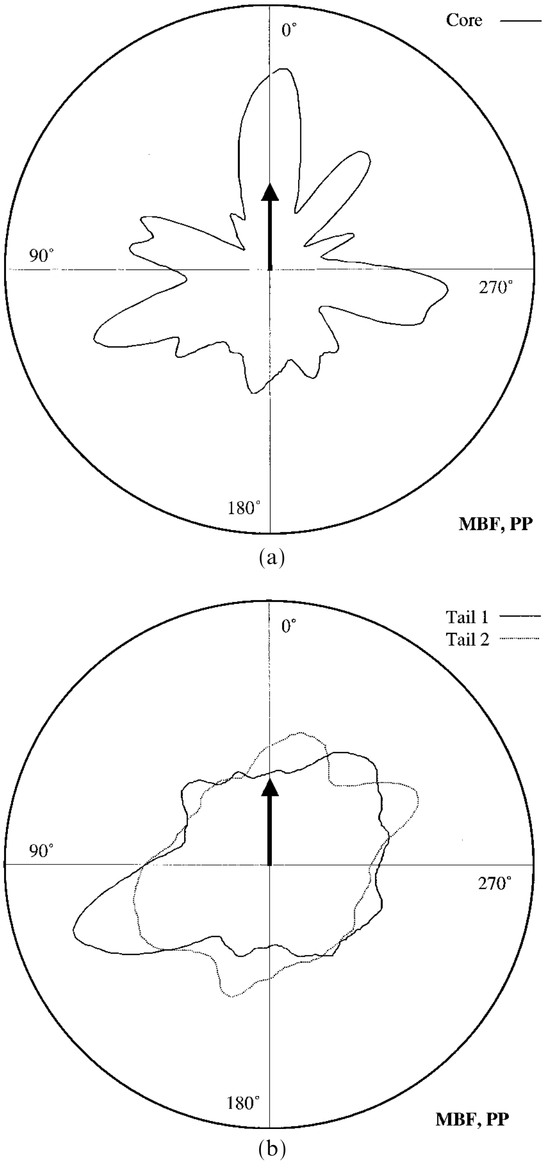


Figure 17. ODFs for (*a*) the core and (*b*) the tails of an isolated MBF molecule on the (1 1 0) surface of PP.

4. Discussion

It is clear from the preceding results that the nature of the alignment found in ferroelectric liquid crystal devices depends on several features of both the substrate and the liquid crystal molecule chosen. The main factors involved appear to be the depth and spacing of any molecular scale corrugations which are found in the polymer surface, the detailed shape of the mesogenic core, and the angles between the alkyl tails and the core. It would appear that the topography of the polymer surfaces, as defined by short range van der Waals forces, is considerably more important than electrostatic interactions in determining the overall behaviour. In this respect, analogies may be drawn with molecular crystals, where it is a general rule that molecular shapes determine the gross features of the crystal structure, while molecular dipoles serve only to modify it [39].

The polymers which produce a clear molecular alignment in our simulations each possess a well defined molecular corrugation. In all cases, this is created by the backbones of the polymer molecules, which form a planar zig-zag conformation, lying side by side in the crystal surface. The differences observed in the quality of the alignment may be related to the depth of these corrugations, which is related, in turn, to the angle between the plane of the polymer chain and the crystal face. The deeper corrugations found on the PVA surface give rise to a narrower distribution of angles for the liquid crystal tails than is found on the PE or Nylon 6 surfaces, and also a more sharply defined set of orientations for the core. The spacing of the polymer chains, in conjunction with the length of the mesogenic core, determines the specific angles which the core is likely to adopt on each surface as it straddles one, two or more chains. However, there is some variation in the precise angles assumed, due to conformational changes within the molecule.

Although in initial simulations it appeared that the orientations of the core were being determined by the requirement for the alkyl tails to lie parallel to the polymer chains [38], careful consideration shows that this cannot be the case. First of all, examination of the peak widths in the ODFs shows that the peaks for the core are narrower than those for the tails in all of the cases considered (see table 2). This implies that the tails possess rather greater mobility than the core, and are thus unlikely to be dictating in which direction it can point. Secondly, simulations involving an isolated core from an MBF molecule showed very similar behaviour to the core within the molecule, albeit with slightly less well defined orientations, suggesting that those orientations observed are inherent to the particular combination of mesogenic core and polymer, and that the presence of the tails serves mainly to stabilize the configurations. Finally, the minimization studies support the idea that the most stable configurations are those with the core straddling one or two polymer chains and the tails lying parallel to the polymer chains. Close examination of the minimization results indicates that the core is able to come into very close contact with the surface in a straddled configuration by adjusting the dihedral angles between the phenyl rings. This is less easy to achieve if the core is lying parallel to the polymer chains.

PP differs from the other three polymers considered, in that the polymer chains assume a helical rather than a planar conformation. Although the chains still stack side by side, they possess substituent methyl groups which line up to form several sets of corrugations running in different directions on the surface. The result is that the liquid crystal molecule is able to adopt many different orientations on the polymer surface, including orientations both parallel and perpendicular to the chains. In experiments, PP is found to induce a homeotropic alignment which may, in fact, be because the roughness of the crystal surface makes it energetically unfavourable for the liquid crystal molecule to lie flat.

While the single molecule simulations are extremely valuable in identifying the type of surface likely to induce orientation, liquid crystal alignment is essentially a co-operative effect, and so it is necessary to examine models containing large numbers of molecules in order to be able to make any quantitative statements regarding preferred alignment directions. The study of MBF monolayers demonstrated the way in which interactions between molecules reduced the degree of configurational variation in the simulation leading to a single preferred orientation for the liquid crystal core and tails. The degree of order in the starting configuration of the system led to small differences in the preferred orientation of the MBF core, but in all cases there was a long range positional order which was a consequence of the registration between the liquid crystal molecules and the molecular level corrugations in the substrate. The degree of positional order in the monolayers was reminiscent of an epitaxially grown crystal layer rather than a bulk liquid crystal phase.

Simulations of liquid crystal bilayers showed a marked difference in order between the layer adjacent to the polymer, and the second layer. It would seem reasonable to suppose that the second layer is more representative of the bulk than the first, and we may use the simulation results to estimate the cone angle for the system. Determination of the cone angle requires us to assume that the hypothetical liquid crystal cell possesses the bookshelf geometry, and that the cone angle is simply given by the construction in figure 2. In this case, the cone angle obtained for MBF on the (1 0 0) surface of PE is $2 \times 10 = 20°$. This may be compared with a figure of 16.2° obtained for rubbed PE surfaces, using other ferroelectric liquid crystal molecules [25]. The figure of 20° should be taken as an upper limit which would be reduced if the smectic layers were not perpendicular to the liquid crystal cell surfaces, as for example in a chevron cell. A more reliable estimate of the cone angle would require more layers of liquid crystals to be simulated, at considerable computational expense.

It has been suggested that large cone angles are normally obtained with polymer surfaces of low symmetry [25]. However, our results do not support this assertion, since the value of cone angle reported above was obtained using a high symmetry face of orthorhombic PE. We would suggest that the low symmetry of the crankshaft-shaped liquid crystal molecule is likely to be far more important in producing large cone angles, and indeed that it is the combination of features from both the surface *and* the liquid crystal molecule that is ultimately responsible for determining the behaviour that is observed.

It should be pointed out that the models described in this paper do not make any attempt to explain the switching process in bistable ferroelectric displays. In our models, the first liquid crystal monolayer is strongly adsorbed onto the polymer surface, and it would seem unlikely that the molecules would find enough free volume to enable them to reorient from one stable state to the other (figure 1). Instead, it is conceivable that the first monolayer remains fixed on the substrate, and that, in the device as a whole, there are many small domains in which the molecules are adsorbed in either one of the two stable orientations. These domains may then nucleate the growth of either stable configuration throughout the cell, depending on the direction of the applied electric field. A considerably larger simulation would be required in order to test such a hypothesis.

One other important feature of ferroelectric devices that has not been considered so far is the liquid crystal pretilt. Large pretilts have been reported from several large scale Gay–Berne simulations of confined liquid crystals [12–15], and it appears that the tilts obtained arise from a competition between the precise nature of the particle–substrate potential and the requirement for a closely packed liquid crystal layer at the interface. We examined our molecular dynamics trajectories to look for evidence for an inherent preference of the liquid crystal molecules to orient away from the plane of the substrate, but could find none. However, it is quite possible that pretilt effects will not become apparent unless the size of simulation is increased, such that the surface layers of molecules are densely packed and in contact with a bulk liquid crystal phase, i.e. conditions consistent with those of the Gay–Berne simulations referred to above. In fact many explanations have been proposed for the generation of liquid crystal pretilt in real devices, several of which require some modification to the polymer surface. It is also possible therefore that successful generation of pretilts in atomistic simulations will require more complex models for the polymer substrate than have been considered here. Large pretilts are important in the production of high contrast ferroelectric displays, and are generally observed in systems incorporating the technologically important polyimide alignment layers. For this reason, the pretilt and alignment of ferroelectric liquid crystals on polyimide surfaces is the subject of a continuing study.

5. Conclusions

Computer simulations have been performed of a ferroelectric liquid crystal molecule, MBF, in contact with several polymer alignment layers. Where alignment of the liquid crystal molecule occurred, it was found to be due to a combination of structural features of both the liquid crystal molecule and the polymer surface. In particular, good alignment was dependent on the presence of a well defined set of molecular level corrugations on the polymer crystal face. An explanation for the origin of the optical cone angle was found, in terms of an off-axial alignment of the liquid crystal core, that appeared to be stabilized by the tendency of the alkyl tails to lie parallel to the polymer axes, but in different corrugations. The isolated molecule simulations indicated that several liquid crystal orientations were possible, with the liquid crystal core straddling different numbers of polymer chains in each case. However, when monolayers of molecules were simulated, packing constraints meant that the orientational possibilities were restricted to just one, in which a single polymer chain was straddled. A cone angle of approximately 20° was estimated from the preferred orientations observed in a system of two monolayers of MBF on PE. This figure is in line with experimental values determined using other liquid crystal molecules.

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