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COMPUTER SIMULATION OF SURFACE ALIGNMENT IN FERROELECTRIC LIQUID CRYSTAL DEVICES

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Abstract Computer simulations have been performed to investigate the behaviour of monolayers of ferroelectric liquid crystals (FELCs) in contact with polymer substrates. The aim of the work is to develop an understanding of the interactions between polymers and FELC molecules, with a view to predicting the size of the optical cone angle, which is an important parameter in determining the performance of FELC displays. We have examined systems consisting of the liquid crystal MBF, which forms a ferroelectric smectic C* phase when suitably doped, and the non-ferroelectric liquid crystal 8CB, in combination with polyethylene and nylon 6 substrates. Molecular dynamics simulations have been performed, initially on isolated liquid crystal molecules and subsequently on small clusters. Although the systems were too small to observe large scale behaviour, such as phase transitions, it has been possible to observe alignment interactions between the liquid crystal molecules and the substrate, allowing estimates of the cone angle to be made. In the systems examined, we have found that the alignment is dominated by interactions between the flexible tails of the liquid crystal and the polymer.

INTRODUCTION

It is well known that the performance of a liquid crystal device is determined by the nature of the alignment layer used. Alignment layers are often made by rubbing a spin coated polymer with a suitable fabric. Nematic liquid crystals are then found to align parallel with the rubbing direction. Two models have been proposed to explain this behaviour. In one, alignment is said to be due to grooves created by the rubbing[1,2] while in the other, the alignment is attributed to rubbing-induced orientation of the polymer molecules in the surface layer of the substrate.[3] Birefringence measurements have shown that the latter model is more likely to be correct.[4]

In ferroelectric liquid crystal (FELC) devices, the alignment process is more complex than in nematic systems. FELC molecules align at an angle to the rubbing direction which is related to the helical cone angle of the FELC, although, for a given FELC, different polymers produce different cone angles. For a working FELC display with optimum contrast, a cone angle close to 45° would be ideal. In practice, cone angles are rather lower than this, usually in the region of 15-25°.

A considerable experimental effort has been expended to understand the orientation mechanism in FELC devices. Myrvold[5], for example, has performed a comprehensive survey of the alignment behaviour of different polymers, and postulates that, for an optimum cone angle, the polymer should be both crystalline and of a low symmetry. There have been few attempts to understand the alignment mechanism at a molecular scale, although two recent computer simulation studies which examined liquid crystals on graphite substrates are of interest.[6-8]

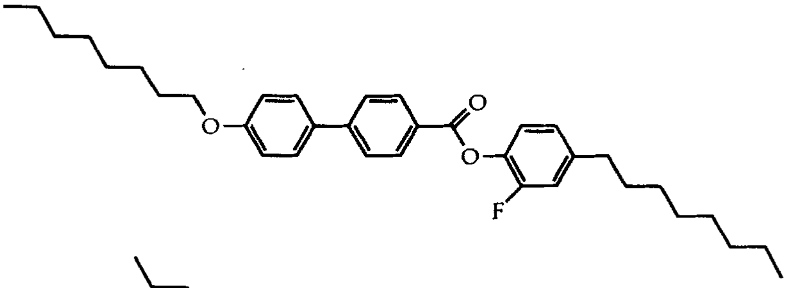
The aim of the present work is to use computer modelling techniques to understand the alignment of ferroelectric liquid crystal molecules on polymer substrates. By determining the preferred orientations of the molecules on a range of polymer surfaces, we aim to predict which combinations of FELC and polymer will produce optimal cone angles. In this preliminary study, we examine the behaviour of MBF and 8CB on polyethylene and nylon 6 surfaces. A mechanism has been found which gives a qualitative explanation for some of the experimentally observed results.

MATERIALS AND METHODS

For our simulations, we have taken the liquid crystal molecule 4-n-octyl-2-fluoro-phenyl 4-n-octyloxy biphenyl-4'-carboxylate, MBF, which forms a ferroelectric smectic C* phase when suitably doped, and the non-ferroelectric 4-n-octyl-4'-cyanobiphenyl, 8CB (see Figure1). Our initial work has been carried out using polyethylene and nylon 6 substrates, because they are the simplest systems which show significant cone angles.[5] We consider the 110 surface of polyethylene and the 100 surface of nylon 6 because these are their dominant crystal growth planes.

Molecular modelling was carried out using the Cerius2 software package.[9] Polymer surfaces were prepared by cutting slices through the crystal, parallel to the required face. Molecular models consisted of either a single or a group of eight liquid crystal molecules, on each polymer surface. Molecular dynamics simulations were

MBF:



8CB:

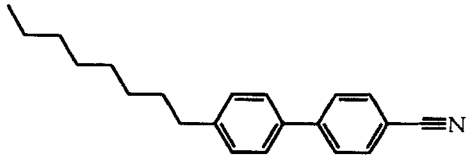


FIGURE 1 The liquid crystal molecules used in the computer simulations.

performed in order to sample the equilibrium configurations of the liquid crystal molecules on the substrates. The microcanonical ensemble was used together with the Dreiding force field[10]. The united atom approximation was used to eliminate all hydrogen atoms. All degrees of freedom in the liquid crystal molecules were allowed to vary, but the polymer substrate was fixed in order to save computer time. Typical simulation times of 1ns were achieved. All simulations were performed at room temperature.

RESULTS

Figure 2a shows a typical configuration of an MBF molecule on the 110 face of polyethylene. It can be seen that the flexible tails of the MBF molecule lie between pairs of polymer chains, taking the positions that additional polymer chains in the bulk crystal would take. Indeed, the orientation of the MBF molecule appears to be governed principally by the interactions between the alkyl chains and the substrate, rather than by any specific interactions between the rigid core and the substrate. The non-linear shape of the molecule means that the two alkyl tails prefer to lie between *different* pairs of polymer chains, so that the rigid core is forced to straddle one or more polymer chains. During the simulation, the molecule explores many different orientations, and Figures 2b and 2c show the distributions obtained for the orientations of the rigid core and flexible tails during one particular simulation. For the cores, a succession of sharp peaks can be seen, which correspond to the rigid core straddling different numbers of polymer chains. For

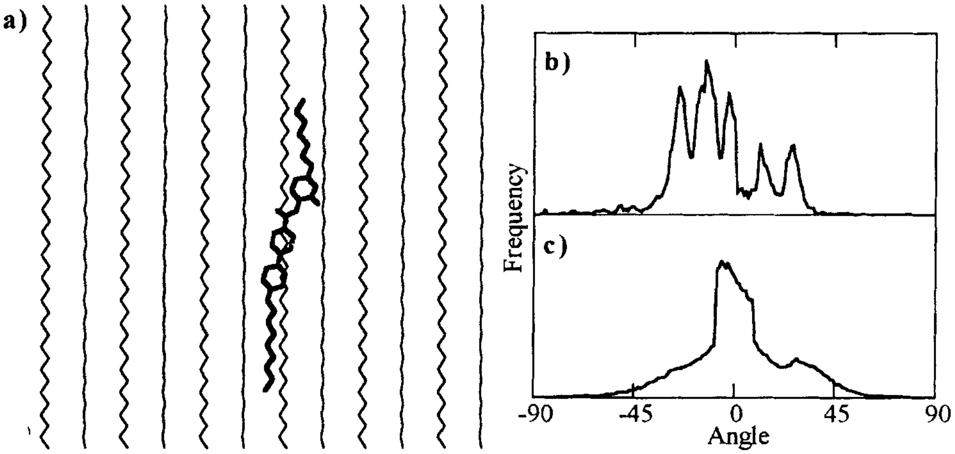


FIGURE 2 (a) An example configuration of an MBF molecule on the 110 crystal face of polyethylene. (b) Orientation distribution for the rigid core of an MBF molecule taken from the same simulation as (a). The polymer chain axis is at 0°. Peaks at ±15° correspond to the core straddling one polymer chain, while peaks at ±30° indicate the core is straddling two polymer chains. A peak close to 0° corresponds to a parallel orientation. (c) Corresponding distribution for the flexible tails, showing a single broad peak parallel to the chain axis.

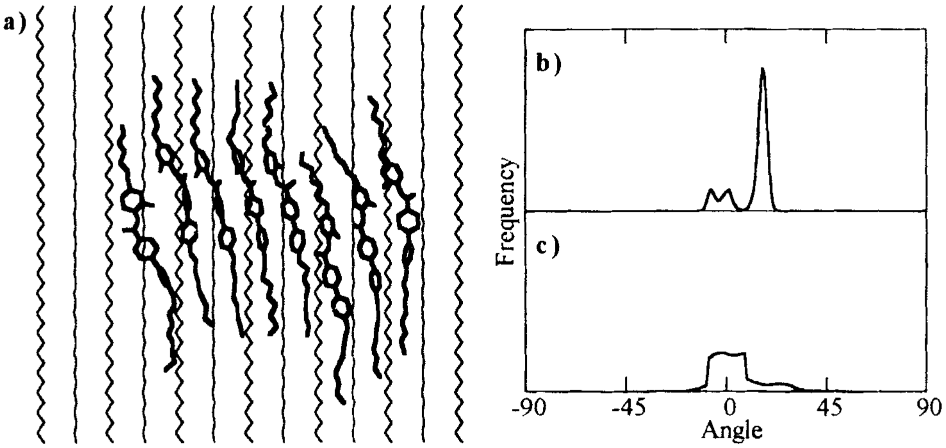


FIGURE 3 (a) Typical configuration from a simulation of eight molecules of MBF on the 110 face of polyethyene. (b) Orientation distribution for the rigid cores of the MBF molecules taken from the simulation in (a). Compared with Figure 2b, it can be seen that the peaks at ±30° have disappeared. (c) The corresponding distribution for the flexible tails showing a single broad peak centred at 0°.

the tails, the main broad peak is centred around the polymer chain direction.

The picture is somewhat different when clusters of MBF molecules are considered. Simulations of groups of eight MBF molecules on the 110 face of polyethylene (Figure 3a) indicate that the presence of neighbouring liquid crystal molecules restricts the orientational freedom, producing a single preferred orientation of the rigid cores with respect to the polymer substrate. This is shown by the distribution in Figure 3b, in which there are two peaks in the distribution equally disposed at ~15° either side of the polymer chain axis, corresponding to the core straddling a single polymer chain. The strong asymmetry in this figure is due to the tendency of the molecules to stick in their preferred orientation.

MBF molecules show similar behaviour on the 100 face of nylon 6, with the flexible tails of the liquid crystal interacting with the CH_2 groups in the polymer backbone. The orientation distribution from a single molecule simulation is shown in Figures 4a and 4b. The rigid core clearly shows a preference for orientations to either side of the chain axis, while the flexible tails are seen to be predominantly parallel to the polymer chains.

8CB was examined as an example of a non-ferroelectric liquid crystal in order to contrast its behaviour with that of MBF. As with MBF, the 8CB molecule interacts strongly with the polyethylene substrate through its single alkyl tail, which shows a strong preference for lying parallel with the polymer molecules (Figure 4d). Since only one end of the liquid crystal molecule is strongly anchored, the rigid core shows a broader distribution of orientations than is the case with MBF, but the mean orientation of the rigid cores is parallel to the polymer chain direction, as would be expected for a liquid crystal in a nematic or smectic A phase (Figure 4c).

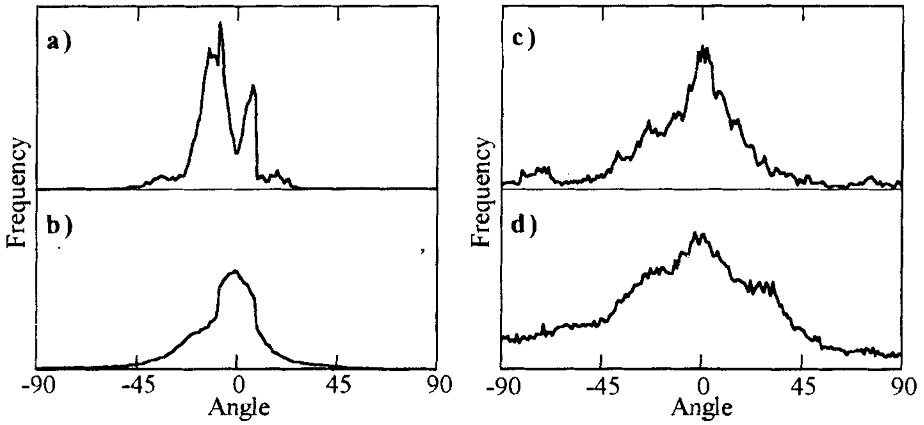


FIGURE 4 (a) The orientation distribution of the rigid core of an MBF molecule on the 100 face of nylon 6, showing peaks either side of the chain axis. (b) The corresponding orientation distribution for the flexible tails. (c) Orientation distribution of the rigid core of an 8CB molecule on a polyethylene substrate from a single molecule simulation. (d) Corresponding distribution for the 8CB tails.

DISCUSSION

The most significant finding from this work is that, in the systems studied, the orientation of the liquid crystal molecules is governed by the interaction of the substrate with their flexible tails, rather than their rigid cores. This appears to be because the tails assume configurations which are similar to those of polymer molecules in the crystal. Thus the resulting orientation of the rigid core is a consequence of several geometric factors, *i.e.* the spacing of the polymer chains in the surface, the length of the rigid core and the angles between the core and the flexible tails. The orientation will also depend on the number of polymer chains straddled by the rigid core and the strength of anchoring of the tails, which will depend on their length.

In fact, as seen in the case of polyethylene, energetically favorable orientations are found for a single MBF molecule with its rigid core straddling 1 *or* 2 polymer chains. To understand how this is possible, it is necessary to realise there will be a certain amount of flexibility in the rigid core, and that the flexible chains will not be perfectly aligned with the polymer axis at all times. However, when a cluster of MBF molecules is considered, molecular packing places further constraints on the possible conformations of the molecules, rendering each more rigid, and eliminating all but one of the favorable orientations.

A naïve approach to determining the cone angle is to equate it with the angle between the preferred orientations of the core, as observed in the simulations. Using the distributions shown in Figures 3b and 4a and assuming a simple "bookshelf" structure, we may place an upper limit on the cone angles for MBF on polyethylene and nylon 6 of around 30°, which is approximately double the experimental value. A more detailed analysis, taking into account molecular pretilt and the presence of chevron defects, would be required to improve this estimate. However, it is clear that this simple approach is capable of providing a qualitative guide to which systems will give the larger cone angles.

Our results appear to contradict the suggestion by Myrvold[5] that a low symmetry surface is required for a large cone angle. However, it would be a mistake to attempt to generalise from our findings, since the orientation observed is a function of both the polymer *and* the FELC molecule chosen. It is quite possible that, in some systems, the orientation will be dominated by the rigid cores rather than by the tails. Studies are in hand to investigate this further.

CONCLUSIONS

We have used computer simulations to examine the interactions of ferroelectric liquid crystal molecules with polyethylene and nylon 6 surfaces. Preliminary results indicate that, in the cases examined, the orientation is determined by a preference for the flexible tails to lie parallel to the polymer chains, and by the geometry of both the liquid crystal molecule and the polymer surface. The cone angles estimated from these simulations are in qualitative agreement with experimental values. More work is needed to explore the generality of our findings.

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