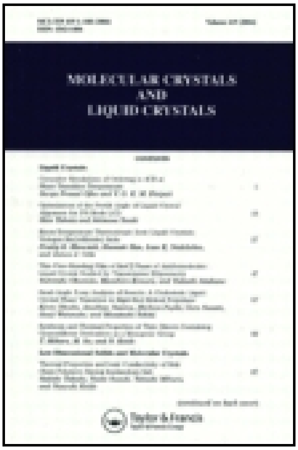

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Molecular Dynamics Simulation of Smectic Phases in Pentamethyl-Disiloxane-Terminated Mesogens

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Molecular Dynamics Simulation of Smectic Phases in Pentamethyl-Disiloxane-Terminated Mesogens

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Molecular dynamics simulations have been used to investigate ensembles of molecules that show smectic liquid crystal phases. We have shown that there is a high tendency for penta methyldisiloxane-terminated mesogens to form assembled dimers, which are then associated into well-defined layers. By applying tilted 3D-boundary conditions we have been able to simulate the formation of a tilted smectic C phase.

Keywords: Simulation; molecular dynamics; siloxane; smectic; tilted layers

INTRODUCTION

Interest in ferroelectric liquid crystals (FLCs) has led to the synthesis of a wide range of new materials with novel molecular architectures. In particular, the pentamethyldisiloxane (PMDS)-terminated mesogens[1-4] have attracted a great deal of interest because of their high smectic C (SmC) phase stability and fast switching times in surface stabilised FLC devices, as either achiral hosts or as chiral dopants. A number of papers have been published[5-6] that attribute the high smectic phase stability to intermolecular polar interactions to give a bilayer structure with PMDS separated regions, as shown schematically in Fig. 1. The proposed structure is based on fitting small angle X-ray scattering (SAXS) data to simple atomistic models.

In this paper we will describe the results obtained from a number of molecular dynamics (MD) simulations on atomistc molecular models, which have been used to probe phase structure in PMDS-terminated organic liquid crystals. In particular, it was interesting to investigate intermolecular interactions between individual molecules in order to probe the proposed assembly of PMDS terminal groups.

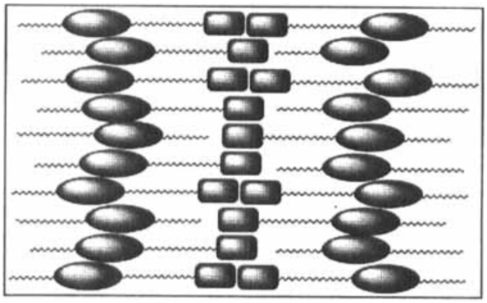
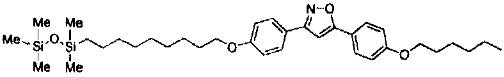


Fig.1 Proposed model for smectic phase formation[5].

EXPERIMENTAL TECHNIQUES

Single atomistic molecules of a heterocyclic liquid crystal[8] possessing a PMDS terminal group (1) were constructed within the Cerius^2 (Molecular Simulations Inc. (MSI)) Visualizer and the geometry optimised using molecular mechanics (MM) and conformational analysis to give the global energy minimum. A Silicon Graphics Indy R4600 workstation with a 100 MHz CPU and 128 MB RAM was used for all simulations. The Universal 1.02 Force Field[9] was used in all cases with a convergence limit of



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5000 iterations or when the 'Standard Convergence Criteria' were reached. These were defined as a 10^{-3} kcal mol^{-1} energy difference and a 3 x 10^{-3} rms displacement of the overall structure. Atomic convergence criteria were set at 0.1 kcal mol^{-1} $Å^{-1}$ in the rms force. The 'Smart Minimizer' function within $Cerius^2$ was applied, which used an initial steepest descents method to remove grossly distorted, high energy structures, then switched to a conjugate gradients method to refine the optimisation.

Dimeric interactions were probed by monitoring the total energy of the two-molecule system while varying the intermolecular separation of various moieties within the common structures. Once a low energy structure was identified, the molecules were placed in close proximity and molecular mechanics used to generate an optimised dimeric structure. MM and MD simulations were performed on ensembles of the dimeric structures. The Crystal Builder module within $Cerius^2$ was used to generate unit cells with dimensions defined by the cell lengths a, b and c and the internal cell angles α, β and γ. A periodic structure was constructed from 27 lattice sites (3x3x3 ensemble) representing 54 individual molecules (5,400 atoms). This was then converted to a periodic superlattice or non-periodic superstructure with boundary conditions defined by $3a$, $3b$ and $3c$. Convergence criteria for MM simulations included an additional term relating to cell parameters which was 0.1 GPa in the rms stress of the system. After performing initial MM calculations on the ensembles, MD simulations were performed. Constant NPT (superlattice) and constant NVT (superstructure) MD were used over 500 steps with a step size of 1 fs to give a total simulation time of 0.5 ps at simulation temperatures between 350 and 400 K. Coupling of the ensemble to a thermal bath, to maintain isothermal conditions, was achieved using the Nosé[10,11] and Hoover[12] (cannonical, extended system Hamiltonian) methods and the T-damping (non-Hamiltonian) method of Berendsen and co-workers.

Electrostatic properties of individual molecules and assembled dimers were probed using the surface generator within WebLab Viewer 2.01 (MSI) using a probe radius of 1.4 Å.

RESULTS AND DISCUSSION

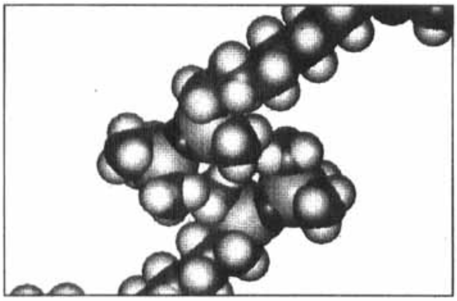

Fig. 2 Expanded PMDS region of dimer
(See Color Plate VI at the back of this issue)

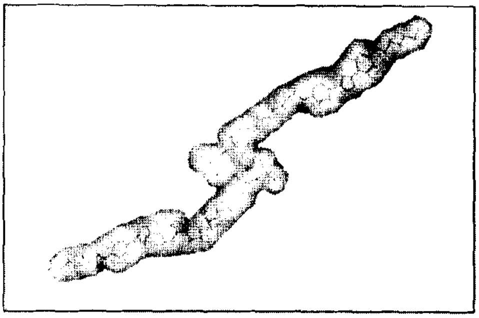

Fig. 3 Electrostatic potential surface of a dimer
(See Color Plate VII at the back of this issue)

Examination of the intermolecular potential in the dimer studies showed there to be a low energy structure in which the PMDS moieties were assembled such that there was minimum steric hindrance. The PMDS region is shown as an expanded CPK model in Fig. 2. We have termed this a 'hand-shake' configuration, as the co-operative assembly of the two PMDS units would appear to stabilise the dimeric structure. The electrostatic potential surface for a complete dimer is shown in Fig. 3. The red regions, located on the heteroatoms of the heterocyclic ring and the aryl ether linkages, indicate areas of highest electron density; the blue areas are electron deficient regions. It is clear from the figure that the PMDS regions are neutral and non-polar, the polar siloxane groups being highly shielded by the low polarity methyl substituents.

MD simulations were performed over a range of unit cell configurations, which were assembled into superlattices or superstructures. Constant NPT MD simulations could only be performed on periodic lattice models (superlattices) owing to the constraints of the software package. Consequently the resulting simulations tended to have a high degree of order and did not reflect the nature of a liquid crystalline phase. Therefore, the majority of the simulations performed used constant NVT MD conditions on ensembled non-periodic superstructures. 3-Dimensional boundary conditions were imposed on the system in the range $3a$ = 99-211 Å, $3b$ = 15-30 Å, $3c$ = 15-30 Å; α = 90°, β = 90°, γ = 45-90°. In all cases a triclinic P1 symmetry operator with primitive lattice centering was applied to the unit cells. An internal angle of γ = 90° was imposed in order to simulate an orthogonal smectic phase and then reduced towards 45° to simulate tilted smectic phases.

An orthogonal smectic phase of the smectic A (SmA) type was simulated when the initial system was set with $3a$ = 120 Å, $3b$ = 21 Å, $3c$ = 21 Å; α = 90°, β = 90°, γ = 90°: T = 360 K. This used a layer spacing of approximately half the overall length of a dimer. A 0.5 ps simulation gave an orthogonal ensemble in which the final layer spacing was calculated as 37 Å with respect to the repeat in the PMDS sub-layer. This was in good agreement with the data obtained from small angle X-ray scattering (SAXS) studies[8] performed on **1**. This represented a small contraction in the a value for the unit cell dimension which was compensated for by a small increase in the values of b to 7.1 Å and c to 8.2 Å. The internal angles remained at essentially 90°.

A tilted phase of the smectic C (SmC) type was simulated when the initial system was set with parameters $3a$ = 111 Å, $3b$ = 21 Å, $3c$ = 21 Å; α = 90°, β = 90°, γ = 45°: T = 360 K. A 0.5 ps simulation gave a tilted ensemble in which the resulting layer spacing (l) calculated along the long axes of the molecules remained close to the initial value of 37 Å with respect to the repeat in the PMDS sub-layer. The final cell parameters obtained after simulation were $3a = 110.8$ Å, $3b = 21.1$ Å, $3c = 21.2$ Å; $\alpha = 90.9°$, $\beta = 89.1°$, $\gamma = 44.2°$. When the system was reoriented so that the PMDS sub-layers were horizontal

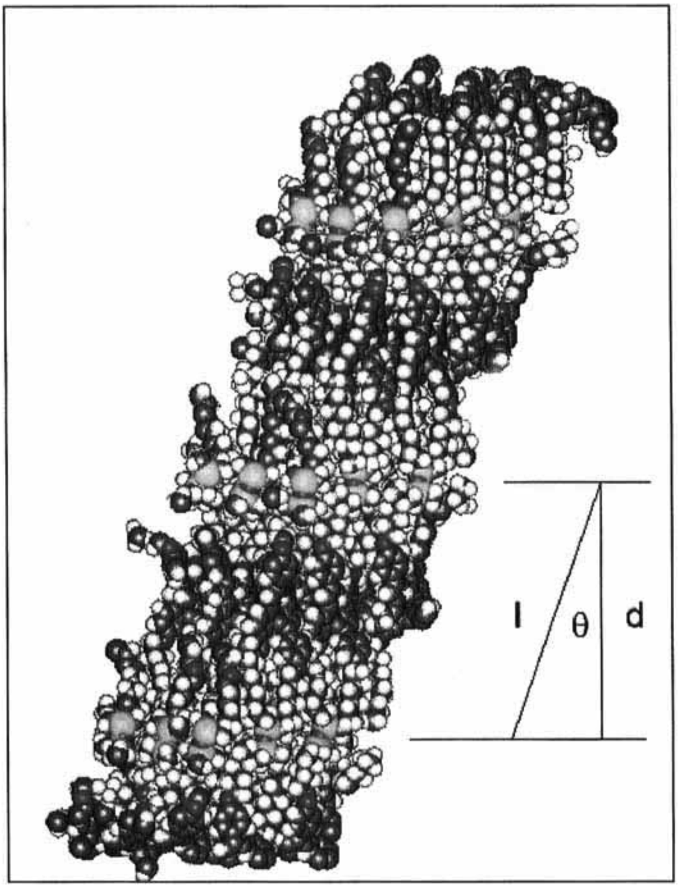

Fig. 4 Tilted smectic layers in the simulation of **1** using tilted boundary conditions
(See Color Plate VIII at the back of this issue)

with respect to the space axes, a tilt was clearly visible and an orthogonal separation of the sub-layers (d) was calculated as 34 Å. This gave the average tilt angle (θ_t) of the molecular long axes relative to the layer normal as 23 ±5°. Again this was in good agreement with the values of both the layer spacing (35.5 Å) and tilt angle (25°) obtained from SAXS studies of **1**. The resulting CPK space filling model representation of the ensemble is shown in Fig. 4, in which the tilted smectic layers are clearly discernable.

A tilted smectic phase was also observed when the third internal angle, γ, was set to 65° thus imposing a molecular tilt of 25°. Again a tilt angle could be calculated from the relationship between separation along the molecular long axis and the orthogonal layer separation of the PMDS units. This was found to be 25 ±5° which is in good agreement with the results for $\gamma = 45°$.

When the molecular separation, as defined by a, was increased to 55 Å while maintaining $b = 21$ Å, $c = 21$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 65°$ a tilted phase was observed with l = 55.1 and d = 46.2 Å. This simulation did not fit with experimental data as the calculated d spacing and tilt angle (33 ±5°) were too large. Additionally, the simulated structure contained large voids within the superstructure so that space was not effectively filled.

CONCLUSIONS

Orthogonal and tilted smectic phases have been simulated atomistically using constant NVT MD on ensembles of 54 individual molecules, costrained by 3D-periodic boundary conditions. Orthogonal boundary conditions give orthogonal smectic A-like layers while tilted boundary conditions lead to tilted smectic C-like layers. The choice of the boundary tilt angle (γ) in the range 25-45° gives little variance in the calculated molecular tilt angle (θ_t) which is found to be close to the experimental value of 25°. Increasing the lengthwise separation of molecules leads to poor simulation structures, while ensuring good packing prior to simulation gives good results. In future work we will be looking to simulate more extensive systems over a wider range of conditions and for significantly longer simulation times using more powerful computational systems.

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