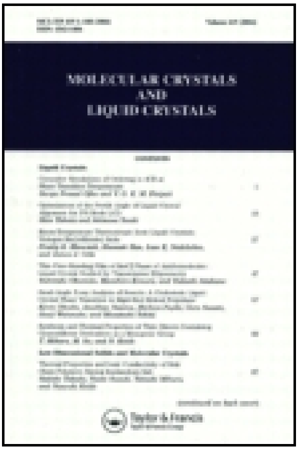

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Makoto Yoneya [a] & Hiroshi Yokoyama [a] [b]

[a] Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba, 300-2635, JAPAN

[b] Molecular Physics Section, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, 305-8568, JAPAN

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Formation of 2-D Chiral Monolayers from Chiral Mesogens Studied with Molecular Dynamics Simulations

MAKOTO YONEYA[a] and HIROSHI YOKOYAMA[ab]

[a]*Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba 300-2635, JAPAN and*
[b]*Molecular Physics Section, Electrotechnical Laboratory. 1-1-4 Umezono, Tsukuba 305-8568, JAPAN*

Monolayer structures of a chiral mesogen, (*R*)- or (*S*)-[4'-(1-methylheptyloxy)-3'-nitrobiphenyl-4yl] 4-(*trans*-5-decenyloxy) benzoate, adsorbed on graphite were investigated with molecular dynamics simulations to clarify the mechanism of chiral supermolecular structure formation. We proposed a mechanism model that is based on the coupling between up-down symmetry breaking and the molecular tilt direction symmetry breaking of the monolayer.

Keywords: chirality; monolayer; symmetry breaking; molecular simulation

INTRODUCTION

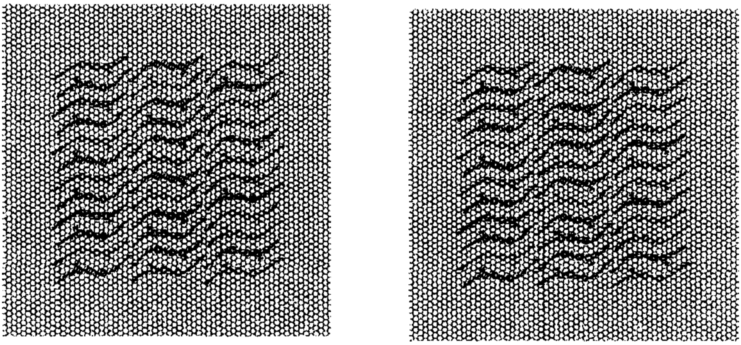
The relationship between supermolecular chirality and molecular chirality is one of the most fascinating subjects in liquid crystal science. Recently, molecular resolution STM images of a chiral mesogen, i.e., (R)- or (S)-[4'-(1-methylheptyloxy)-3'-nitrobiphenyl-4yl] 4-(*trans*-5-decenyloxy) benzoate (MHNBDB), adsorbed on the basal plane of graphite were obtained as a crystalline monolayer with packing chirality in two dimensions (2-D) [1]. The observation reveals that the molecular in-plane tilt directions with respect to the layered 2-D crystalline structure are reversed with the change in molecular chirality, i.e., clockwise (CW) and counterclockwise (CCW) with R- and S-MHNBDB, respectively. However, the mechanism of the chirality transformation from molecular to supermolecular structure is not yet clear. In this study, we tried to clarify the mechanism with a molecular dynamics (MD) simulation approach.

MODEL AND METHOD

The MD simulations were done with a cluster of 36 MHNBDB molecules placed on the basal plane of graphite with 2-D periodic boundary conditions. To introduce the molecular chirality, a detailed atomic model was used. All hydrogen atoms in CH_n groups were treated as "united" atoms, except the hydrogen atoms that were attached to the chiral carbon atom of the MHNBDB molecule. The MHNBDB molecule was treated as a flexible model, except for all bond stretching degrees of freedom, whereas the graphite layer was considered to be rigid and only a single layer was considered for simplicity. The inter- and intra-molecular interaction potential function employed was the GROMOS potential [2], and some additional parameters specially required for MHNBDB and graphite were taken from the literature [3, 4]. Atomic charges were obtained from semi-empirical molecular orbital calculations using the program MOPAC-PM3 and a $1.8nm$ charge-group based cutoff was applied for non-bonded electrostatic and van der Waals interactions. Trajectories were produced by time integration with the leap-frog algorithm by using a $1fs$ time step. The non-iterative matrix method [5] was used to constrain all bond lengths of the MHNBDB molecules. After short steepest descend energy minimization and initial MD runs, $1ns$ production MD runs were carried out at constant temperature around 300K by using weak coupling to a heat bath [6].

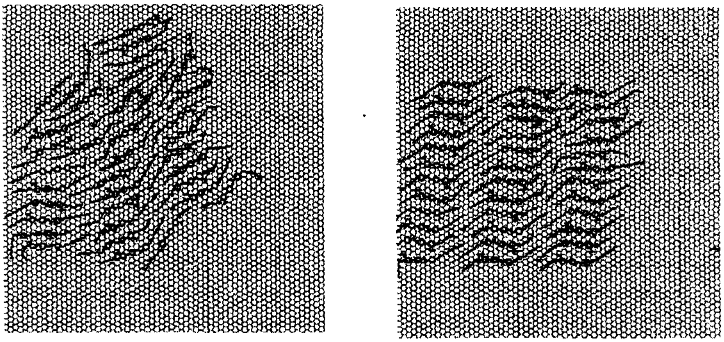
RESULTS

First, we did the MD runs from two initial structures with only the molecular chirality of the MHNBDB molecules being different (i.e., (R)- and (S)-MHNBDB). These initial structures (fig. 1) were made with reference to the proposed model structure (and the lattice constants) from STM observations [7], but without mesogen core tilt in order to see the molecular chirality dependent spontaneous tilting in the course of MD simulations. The snapshots after $1ns$ MD runs are shown in fig. 2. The major difference was not the tilting directions as expected, but the stabilities of the initial lattice structures. In the MD run from the initial structure shown in fig. 1(a), the initial lattice structure was quickly (within a few tens of picoseconds) destructured, while in the run from the structure shown in fig. 1(b) the basic lattice was kept up to $1ns$. Relatively large structural change in the former case originated in conformational change of individual MHNBDB molecules. The difference in molecular chirality between these two initial conditions appeared as the relative positions of hydrogen



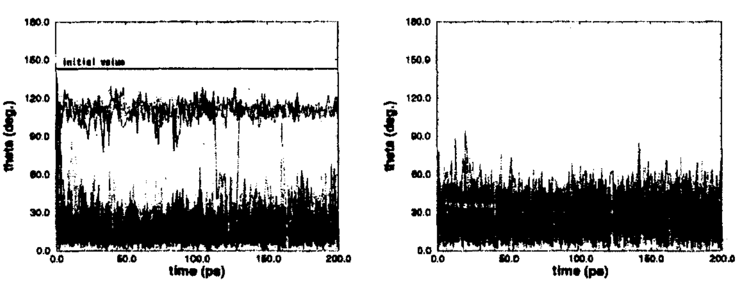
(a) (b)

Figure 1 Initial structures with (a) (*R*)- and (b) (*S*)-MHNBDB



(a) (b)

Figure 2 Snapshots after 1*ns* MD runs for (a) (*R*)- and (b) (*S*)-MHNBDB



(a) (b)

Figure 3 Time evolution of bond directions for (a) (*R*)- and (b) (*S*)-MHNBDB

and "united" methyl (CH_3) atoms attached to the chiral carbon (C^*). As a result, the C^*-CH_3 bond was directed toward the graphite surface for the (*R*)-MHNBDB (fig. 1(a)), whereas it was in the opposite direction for the (*S*)-MHNBDB (fig. 1(b)). Time evolutions of these C^*-CH_3 bond direction angles from the graphite surface normal are plotted in fig. 3 for the initial 200*ps* MD runs. In contrast to the case of (*S*)-MHNBDB, in which the C^*-CH_3 bond directions were kept around the initial direction (upward relative to the graphite surface), in the case of (*R*)-MHNBDB, initially downward directed C^*-CH_3 bonds were quickly rotated upward, except for some intermediate state molecules. This rotation was accompanied by relatively large conformational fluctuations which resulted in destruction of the initial lattice structures as shown in fig. 2(a).

The stability difference of the initial structure did not directly originate from the molecular chirality, but just depended on the initial C^*-CH_3 bond directions relative to the graphite surface. To confirm this, we did an MD run starting from the same initial structure (with (*R*)-MHNBDB) in fig. 1(a), but turned the mesogen monolayer upside-down which made the C^*-CH_3 bond point upward. We found that the initial lattice structures were basically kept up to 1*ns*. These simulation results clearly show the presence of adsorption selectivity (surface activity) for the graphite surface that discriminated the sticking-out direction of the methyl group from the chiral center. This selectivity brake the up-down symmetry of the monolayer in a distinct way, depending on the molecular chirality. However, even for the structure in which the initial lattice structure was

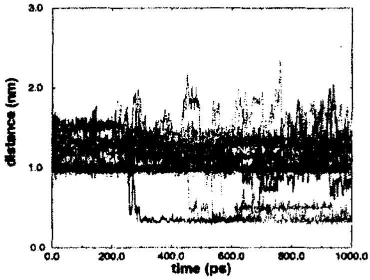
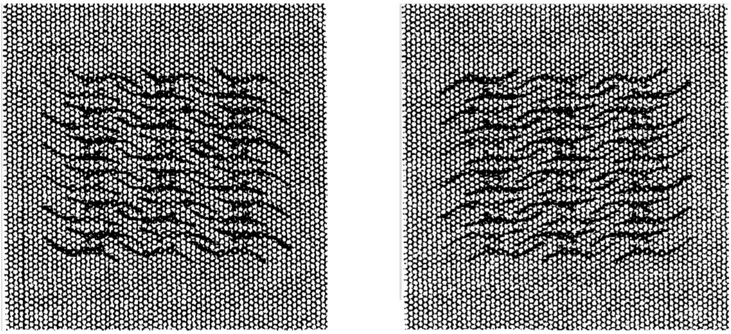


Figure 4 Time evolution of nearest-neighbor distances between nitrogen atoms

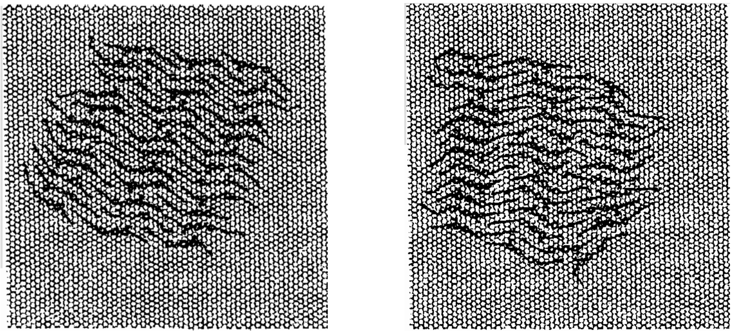
almost completely kept (i.e. fig. 2(b)), the mesogen core tilt was small and moreover, in the opposite direction compared to the STM image (i.e., around 30° and CW for (*R*)-MHNBDB, respectively).

So, some modification of the model monolayer structure was required. We found a different type of antiparallel MHNBDB dimers in the MD run from the initial structure in fig. 1(b). We plotted the temporal change of the distances between the nearest-neighbor nitrogen atoms in the mesogen monolayer in fig. 4. Most of the distances were around 1.2nm which corresponded to the initially placed antiparallel dimer configuration, but a few stable pairs showed closer distances which meant spontaneous formation of dimer pairs in which the nitro-groups of MHNBDB molecules were closely associated. Using this dimer structure as a structural unit, we again did MD runs from two initial structures (shown in fig. 5) in which molecular chirality of the MHNBDB molecules were different and also the up-down of the monolayers were set like the C*-CH$_3$ bonds directed upward (then, the molecular zig-zag directions were different). In these MD runs, mesogen cores were spontaneously tilted in different directions depending on their molecular chiralities. The snapshots after the 200ps MD runs are shown in fig. 6. Obtained mesogen tilt directions (CCW and CW for (*R*)- and (*S*)-MHNBDB, respectively) and the angles (around 30°) were in good agreement with the STM observations. These results suggested that the nitro-group associated dimers would be more probable units in the adsorbed MHNBDB monolayer. Although the association of the nitro-group which has a large dipole moment implied dipole pair-interactions would be the origin of this tilting, the tilting was



(a) (b)

Figure 5 Initial structures with nitro-associated (a) (R)- and (b) (S)-MHNBDB



(a) (b)

Figure 6 Snapshots after 200ps MD runs for nitro-associated (a) (R)- and (b) (S)-MHNBDB

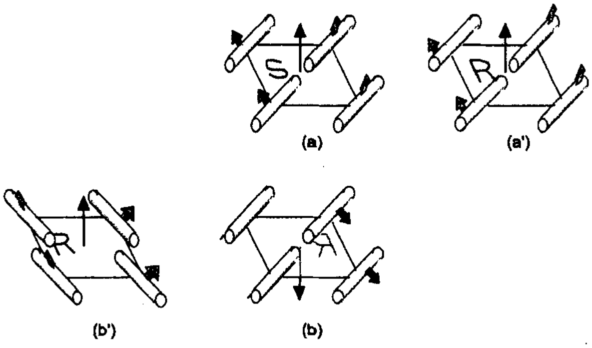


Figure 7 Chiral phase separation model

observed in the trial MD run without any charges on the nitro-groups. Hence, we considered the tilting basically originated from a steric effect of the nitro-group to gain a higher packing fraction as a condensed state.

DISCUSSION

According to the MD results, we propose a model (fig. 7) to explain the origin of the chiral supermolecular structure formation that is based on the coupling between the up-down symmetry breaking and the molecular tilt direction symmetry breaking. As in the previous section, the tilt direction symmetry is broken by the steric effect with the nitro-group. In such a tilted mesogen monolayer, the C*-CH_3 bond directions break its up-down symmetry, and the monolayer configuration with the bond upward, as shown in fig. 7(a) for the case of (*S*)-MHNBDB, was selected for the surface activity. If we change the molecular chirality to (*R*)-MHNBDB, then, all the C*-CH_3 bonds now are directed downward, and the up-down of the monolayer is reversed as in fig. 7(b). Again, due to the surface activity, this monolayer should be upside-down, and this results in the molecular tilt direction being reversed to CCW as in fig. 7(b'). Consequently, one-to-one correspondence between absolute molecular chirality (*R* or *S*) and monolayer 2-D chirality (CW or CCW tilt direction) can be explained with this simple model.

In the model above, the coupling between the two origins of symmetry breaking is defined by the geometrical conformation of the molecule.

Thus, a systematic change of molecular geometry would cause an alteration of the one-to-one correspondence between molecular- and supermolecular chirality. As an example, we consider the monolayer while moving the chiral center down the alkyl chain by one unit, but keeping the C^*-CH_3 bond up-down direction the same, as in fig. 7(a'). In this case, the molecular chirality is alternatively reversed, but supermolecular chirality is unchanged. Then, the one-to-one correspondence (i.e. coupling) between molecular- and supermolecular chirality is alternatively changed with this chiral center move. At least in the case of a one-unit chiral center move, we confirmed it with the MD simulation. In the opposite sense, the 2-D chirality of the monolayer would alternatively be reversed by moving the chiral center down the alkyl chain by one unit, but keeping the molecular chirality the same. This would be especially interesting when we consider the similar "odd-even" effect on twist sense reversal in the bulk chiral nematic materials [8] which has been known as unexplained phenomenon.

Acknowledgments

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