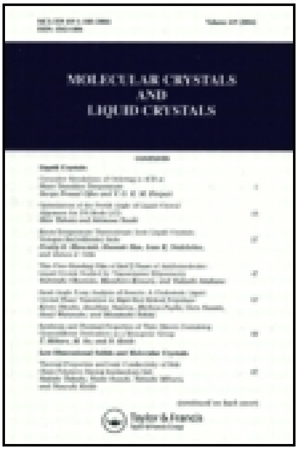

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Structure, Stability and Response to the Electric Field of Antiferroelectric Smectic Materials

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Structure, Stability and Response to the Electric Field of Antiferroelectric Smectic Materials

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The structure and switching of five antiferroelectric mesogens are studied by the constant temperature-pressure molecular dynamics simulation. The conformations of the end chains in the smectic phase are compared with those at an isolated single molecule estimated by the method of molecular orbitals, where the bending angle of the chiral chain as well as the angle of the achiral one is shown to be enhanced. The tilt angles obtained here are in well agreement with the experimental ones. The response of the anticlinic alignment to the transverse electric field is also tested.

Keywords: antiferroelectric smectics; MD simulation; molecular conformation; synclinic alignment; anticlinic alignment; switching

INTRODUCTION

An antiferroelectric smectic phase is one of the most important findings in liquid crystal field in this decade.[1] Various interesting phenomena, that is, successive phase transitions and hysteresis-free response, have been observed therein and the origin of such phenomena is attributed to the competition between the ferroelectric and antiferroelectric interactions with frustrating long range character of interactions.[2-4] From the application point of view, so far, we have only trial pieces of display to utilize antiferroelectric materials.[5,6] One of the technical points to be overcome is a realization of low switching voltage.

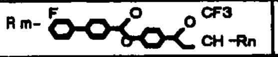
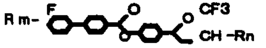
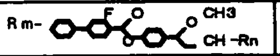
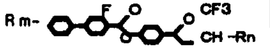
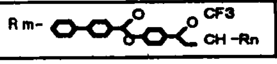
Lately, we have tried to elucidate the stabilities of the layer structure and the shape of molecules of various antiferroelectric smectic materials containing fluorine atom[7] using a software package MASPHYC (Fujitsu Co., Ltd.)[8] for the molecular dynamics simulation (MD), which has been shown to be of use in an investigation of liquid crystals.[9] In the previous study, bending angles of a chiral chain are shown to be suppressed while the angle of an achiral ones are enhanced comparing with those at an isolated single molecular state estimated by the method of molecular orbitals. However, the simulated system is composed of 32 molecules, which is too small to obtain reliable results.[7]

We study again the same problem at the system with 128 molecules for five kinds of materials, two of which are chosen from the ones studied previously. By applying the transverse electric field, the change of the anticlinic alignment is also executed to test the stability of the phase and switching behaviour.

MODEL SYSTEM AND CONDITIONS OF SIMULATION

The five antiferroelectric materials are chosen (synthesized by Syowa

TABLE 1 Antiferroelectric smectic materials.

Material	Core part	Chiral chain Rn		Achiral chain Rm	
		n	ϕ_c	m	ϕ_a
1		4	49. 4	9	22. 9
2		6	38. 0	10	21. 9
3		6	35. 7	9	14. 9
4		6	40. 9	9	14. 7
5		6	42. 0	9	28. 2

Shell Sekiyu Co., Ltd.) with the intention of comparing the properties with molecular components systematically as listed in Table 1, where angles of end chains from a core part at an isolated molecule are estimated as before by the method of molecular orbitals (MO). The magnitude of a dipole moment per molecule is in a range, 4.0-6.1D (see Fig. 3). All of these materials exhibit the antiferroelectric phase at room temperature.

At the simulation, molecules are constructed from atoms interacting with the intramolecular potential V_D, called DREIDING potential,[10] consisting of four types of bonding potentials, for stretch, bend, twist and oscillation, showing the deviations from the stable configuration of an isolated molecule obtained by MO. Every MD cell system is composed of 128 molecules, in which molecules interact to each other with the pair potential V, a combination of Lennard-Jones potential and Coulomb interaction acting among atoms. The magnitude of the electric charge is calculated by MO for each materials. By using this data together with the configuration of the isolated molecule above mentioned, all of parameters appearing in these potentials are determined by the program in MASPHYC.

Initially, the molecules are aligned regularly in two layers containing 64 molecules for each, in which several types of molecular configurations are taken.[7] The periodic boundary condition is applied to every MD cell boundary. The simulations are carried out under the conditions of constant temperature, 300K, and of constant pressure, 10^5Pa. The time step interval is chosen to be 0.5fs and total running steps is 1.5×10^5 steps, corresponding to the real time 75ps. For an anticlinic layer stacking a transverse electric field is applied in the tilt direction within the smectic layer at the time steps 5×10^4 in the middle of the execution, where the magnitude is 2×10^8V/m, which corresponds to several ten times what we usually apply. The reason for choosing such a large value is to compensate the shortness of simulation time. The cut-off distance of the interaction is 10 angstrom, while the Coulomb potential is estimated by the sum of Ewald method without cut-off. The equations of motion of particles are solved utilizing MASPHYC with Gear algorithm.[8]

RESULTS

The layer structure as well as the molecular configuration at the final stage of the simulation depends seriously on the initial configuration because of, probably, the shortness of the simulation time step. Here, referring to the results of previous simulations,[7] a certain configuration for each species of molecule is chosen, from which configuration with well aligned anticlinic structures is expected to be finally achieved. Similarly, the synclinic alignment is also simulated, though the switching simulation is omitted.

The tilt angle of the core part of molecules is plotted to the experimental value at the antiferroelectric phase[7,11] in Fig. 1, where the circle (○) denotes the tilt at the anticlinic configuration without the field, the closed circle (●) the one at the final state and the triangle (△) the one at the synclinic alignment. Those in the anticlinic alignment agree well to the experimental ones, and remarkable changes from those to the final

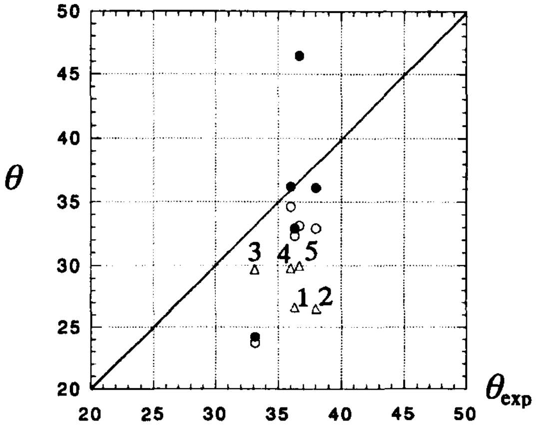
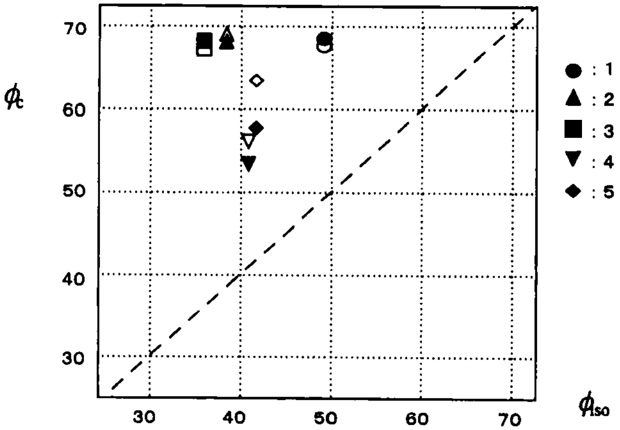
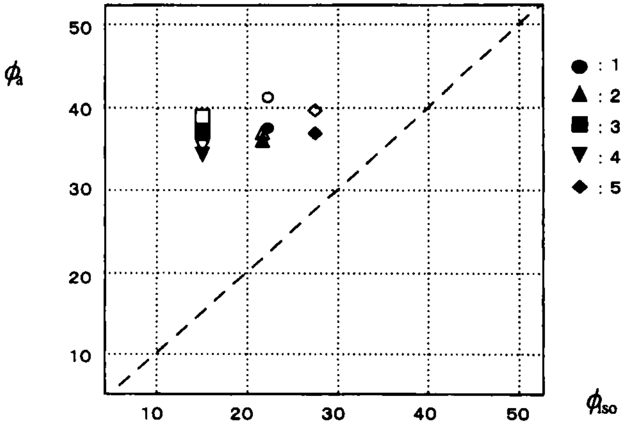


FIGURE 1 Tilt angle θ compared with experimental one θ_{exp}

values in the electric field are not observed for all of materials except for molecule 5. In Fig. 2, the bending angles of molecular end chains ϕ at respective states are compared with the ones at the isolated molecular state ϕ_{iso}, where hollow symbols denote the ones at the anticlinic alignment and the filled ones are at the final state in the electric field. All



(a) chiral chain



(b) achiral chain

FIGURE 2 Bending angles of end chains

of these are larger than respective ones at the isolated state. This result contradicts to the previous one at the chiral chain, that is, the bending angles of chiral chain at the smectics are estimated previously to be smaller than the ones at the isolated molecular state though the data are dispersed,[7] while at the achiral chain present result is similar to the previous one. It is noticed that the same value of pressure is taken at each simulations. In the present stage it is plausible to adopt the present result because of the largeness of system though we have no logical ground.

Here, the response to the electric field is mentioned. At molecules 2, 4 and 5, a change of the anticlinic stacking to the synclinic one occurs, while at molecules 1 and 3 drastic structural change is not observed up to 1.5×10^5 steps. In Fig. 3, the values of electric polarization per molecule, p, at the anticlinic stacking and final stage of the response together with the one at synclinic stacking are shown in relation to the dipole moment of the isolated molecule, p_{iso}, where the numbers indicate the species of molecules and marks ○, ● and △ are common to those in Fig. 1. Even in the anticlinic stacking, that is, the antiferroelectric structure, a spontaneous polarization never disappears and the ratio p / p_{iso} amounts to

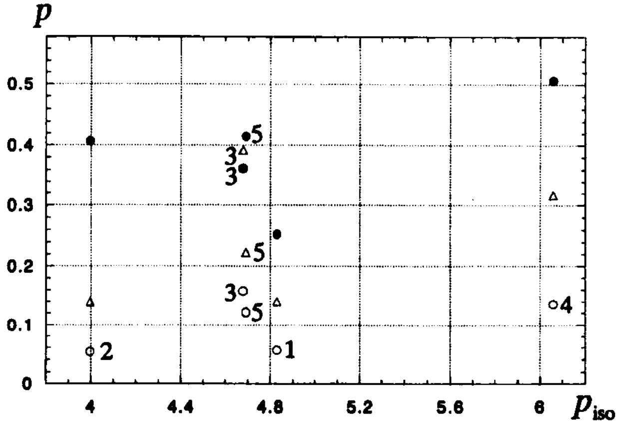


FIGURE 3 Electric polarization versus p_{iso}

3% for molecules 3 and 5 and 1-2% for others because of the fluctuation or the incompleteness of layer ordering, while at the synclinic stacking the ratio is in the range 3-8%. For molecules 1 and 3, the spontaneous polarization in the electric field reaches 5% and 7.7% of p_{iso}, respectively, nevertheless the remarkable change of stacking is not observed, while for molecules 2, 4 and 5 the polarization amounts to 8.4-10%.

SUMMARY AND DISCUSSION

By constant temperature-pressure molecular dynamics simulations molecular structure, tilt angle at the smectic ordering and response of the anticlinic stacking of molecules to the transverse electric field are studied for five species of antiferroelectric materials containing fluorine atom utilizing software program package MASPHYC. The layer structures of anticlinic and synclinic alignments are reproduced, where tilt angles are in well agreement with the experimental ones. The bending angles of the chiral and achiral chains in the layer structure are larger than the one at respective isolated molecular state for all mesogens tested here. The response of the anticlinic stacking to the transverse electric field in the tilt direction is also studies, where change from anticlinic structure to the synclinic one is observed to occur at molecules 2, 4 and 5, while no structural change occurs at molecules 1 and 3. The spontaneous polarization at the synclinic structure is estimated at most 5% of the value at the isolated molecule except for the molecule 3 with 8%, and the one at the final state from the anticlinic one in the electric field is in the range 5-10%. Anyway, it is appropriate in the present stage to conclude that the results about the response are preliminary because of the shortness of the simulation steps.

In the present investigation the antiferroelectric mesogens are chosen to compare the results to the radical groups of molecules systematically, while quantitative data reliable to be compared are not obtained here.

However, accumulation of such studies as the present one is required to clarify the complicated phenomena in liquid crystals, especially, from the molecular stand point of view. As to the present study, the improvement of the simulation steps as well as the number of molecules is expected in the ordinary way.

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