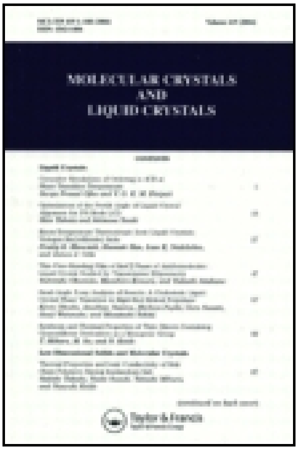

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MD Simulation of Bent Gay-Berne Molecule Systems; Molecular Shape and Flexibility

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MD Simulation of Bent Gay-Berne Molecule Systems; Molecular Shape and Flexibility

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Molecular dynamics simulation is carried out at the system of bent molecules to study the effects of a molecular bend and flexibility to the liquid crystalline ordering. The molecule is a dimer of two types of Gay-Berne particles connected by a harmonic spring at each ends and makes a given angle in the energy minimum at an isolated state. A decrease of clearing temperature with an increase of the bend angle is depicted. By changing a strength of the spring constant, an influence of flexibility to the ordering is studied, where the clearing temperature shows a sigmoidal curve for the spring constant and the nematic ordering is hardly observed in the soft limit. To see the another effect of molecular shape to the ordering, two types of different combinations of length of the constituent Gay-Berne particles are introduced and ordering behaviours are tested.

Keywords: bent molecule; biaxiality; flexibility of molecule; Gay-Berne model; MD simulation

INTRODUCTION

An appearance of liquid crystal phase is due to an anisotropic interaction, which comes from the shape of the constituent molecules. So, it is an interesting problem how the liquid crystalline ordering depends on the shape of molecule. For example, the shape of the tail [1] and the bent of molecule [2] work a serious part in the order of antiferroelectric smectics [3]. In the theoretical point of view, the model systems such

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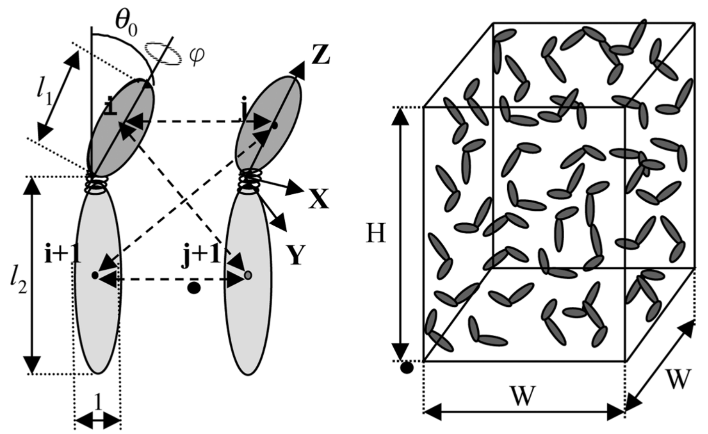
as Gay-Berne model (G-B model) [4] are convenient to elucidate the formation of liquid crystalline ordering.

In the previous work, the present authors have studied the ordering of the system of bent molecules which are dimer of two kinds of Gay-Berne particles (G-B particles) connected by a harmonic spring at each ends making a given angle at an isolated molecular state [5]. Molecular dynamics simulation suggests a strong dependence of the clearing temperature T_c on the bend angle. The effect of permanent dipole attached to the molecule is also reported recently [6]. However, the previous study free from the dipole moment [5] is preliminary because the chosen values of bend angle are restricted rather to few values of large ones. Here, by the constant temperature–volume molecular dynamics simulation (NTV MD) the dependence of T_c on bend angle is studied in detail, where values of bend angle are chosen in the interval of 5° in the region of small angle. By changing the strength of spring, dependence of the ordering on a molecular flexibility is studied, and an effect of molecular length together with the shape of molecule is tested by introducing another combinations of constituent G-B particles.

MODEL AND CONDITION OF SIMULATION

NVT molecular dynamics simulations are carried out for the system of bend molecules which consist of two G-B particles coupled by harmonic spring. Three types of combinations of two G-B particles are studied; the combination of lengths are 3 and 2 in the unit of a diameter a (Model I), 3 and 3 (Model II) and 4 and 2 (Model III). The potential energy is the sum of individual Gay-Berne potential (G-B potential) between particles of inter-molecules and stretch, bend and twist deformation energies of intra-molecule as shown in Figure 1(a). The interaction parameters of G-B potential are chosen after those used preciously [6–8]. The bend angle θ is given as θ_0 at energy minimum in vacuum. Force constants K_s, K_b and K_t, for stretch $K_s\ \delta^2$, bend $K_b\ (\cos\theta - \mathrm{cosq}\ \theta_0)^2$ and twist $K_t \cos^2\phi$ of molecular deformations, are chosen as $5a^{-2}$, 1.0 and 1.0, respectively in the unit of G-B potential strength ε_0. In the latter part of simulations, K_b is changed to see the effect of molecular flexibility to the liquid crystalline ordering.

The shape and size of system is shown in Figure 1(b), where the periodic boundary condition is applied at each wall of MD cell. Models and MD cell are summarised in Table 1, and conditions of simulations are given in Table 2.



(a) **(b)**

FIGURE 1 Model of molecule and MD cell.

At the beginning, molecules are generated randomly at high temperature $T = 10$ (in the unit ε_0/k_B, k_B the Boltzmann constant) in order that molecules do not overlap to each other, and the simulation is carried out at that temperature up to 10^5 time step to relax

TABLE 1 Models

		MD-Cell		
Model ($l1$–$l2$)	Molecule	W	L	N
I	3–2	12	22	512
II	3–3	12.6	23	600
III	4–2	12.6	23	600

N: Number of molecule in cell.

TABLE 2 MD Conditions

MD ensemble	NVT
Algorithm	Verlet
Time step (sec)	$10^{-15} \sim 10^{-16}$
Temperature (kT/ε_0)	$10 \rightarrow 0.1$
Force cut-off	8.0
Density	~ 0.3

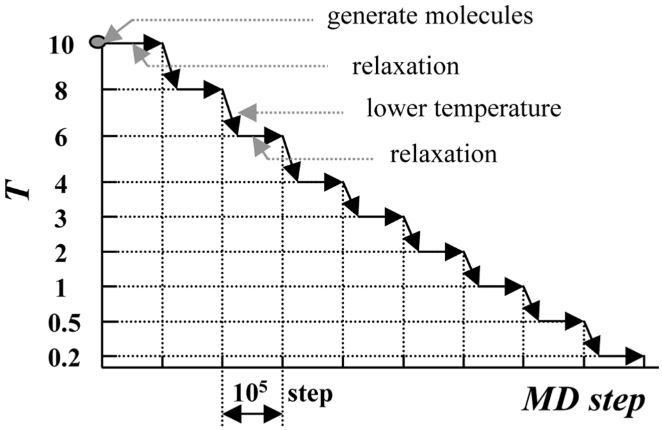


FIGURE 2 Procedure of MD simulation.

the configuration of system, where the molecular dynamics step is chosen to be 10^{-15}sec. After that the temperature is reduced gradually from 10 to 0.2 (in some cases, 0.05) at a rate as shown in Figure 2. The data are taken as averages during 10^3 time step of final stage at each temperature. Model I is chosen as a representative model and the value of θ_0 is changed from 0° to 60° in an interval 5° up to 30°. At the angle 15° the spring constant K_b is changed to see the effect of molecular flexibility. Simulations for the systems of Model II and Model III are are also carried out to study the effect of molecular length at $\theta_0 = 15^\circ$ and 30°.

RESULTS

First, ordering processes of the system of Model I with typical values of θ_0 are explained. Snap shots of the system with $\boldsymbol{\theta}_0 = 15^\circ$ are shown in Figure 3, as the case of small bend angle, where the system is isotropic with nematic order parameter $S = 0.09$ at $T = 5$ in (a). The nematic order parameter is the usual one determined from an average of the tensor $(n_{i\alpha}n_{i\beta} - \delta_{\alpha\beta}/3)$ with unit vector $\boldsymbol{n_i}$ connecting the centres of gravity of G-B particles in i-th molecule. The clearing temperature T_c is determined at which $S = 0.4$, and we obtain here $T_\mathrm{c} = 2.4$. The snap shot of nematic phase at $T = 1.5$ is shown in Figure 3(b) where $S = 0.6$. As the temperature is lowered, the system shows the smectic phase as shown in Figure 3(c), where $T = 0.2$, $S = 0.95$, smectic order parameter $\sigma = 0.22$ and tilt angle $\gamma = 7.0^\circ$, where σ is McMillan's order parameter defined as an average of $\cos(2\pi z_i/d_0)(3\cos^2\nu_i - 1)/2$ with z_i

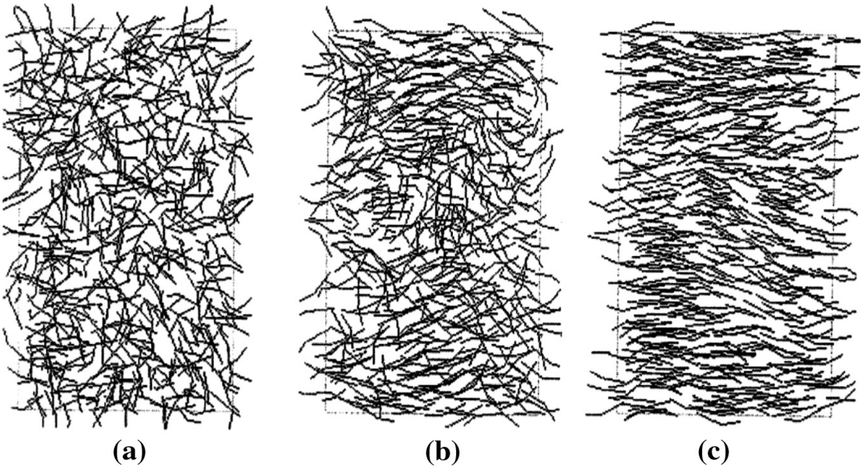


FIGURE 3 Snapshot of Model I with $\theta_0 = 15^\circ$; (a) isotropic phase ($T = 5$), (b) nematic phase ($T = 1.5$), (c) smectic phase ($T = 0.2$).

the coordinate along the nematic axis, ν_i the angle of $\boldsymbol{n_i}$ making from the nematic axis and d_0 thickness of smectic layer. Though γ takes a finite value, the phase is considered to be a smectic A phase because of the small value of γ and smallness of the present system size.

As θ_0 increases, the nematic ordering is suppressed. Profiles with large bend angle at low temperature region ($T = 0.05$) are shown in

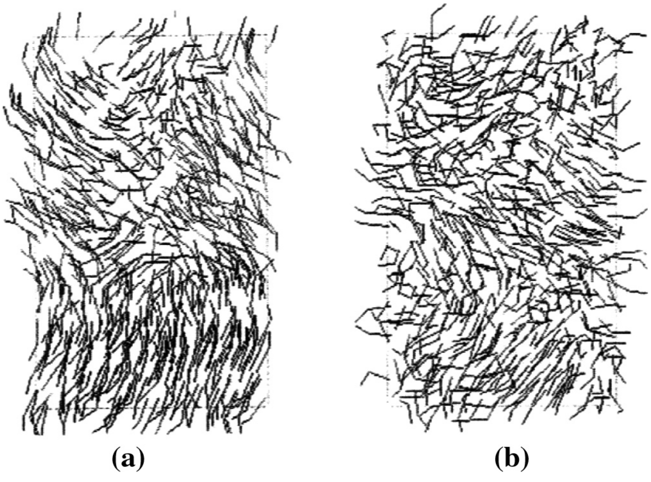


FIGURE 4 Snapshot of Model I at low temperature ($T = 0.05$); $\theta_0 = 45^\circ$, (b) $\theta_0 = 60^\circ$.

Figure 4, where $\theta_0 = 45^\circ$ (a) and 60° (b). Both systems change from isotropic phase to something like ordered one near $T = 0.2$, which look like multi-domains of smectic order (called here as multi-domain phase). It is known experimentally that bent-core mesogens form circular domains, in case they do not have the nematic phases [9,10]. It is quite interesting whether the multi domain phase truly represents the circular domains or not. However, in the present stage, we cannot certify this point concretely, because of the smallness of the present system and lack of detailed study of system of molecules with large bend.

For various values of θ_0, T_c is determined as shown in Figure 5, where the decrease is observed near $\theta_0 = 20^\circ$. Here, biaxial order parameter S_b is evaluated as an order of the second molecular axis as shown in Figure 6, in which the values together with S and σ achieved at the final stage of each MD simulation are shown. We see a clear change of ordering properties near $\theta_0 = 30^\circ$. In the side of small bend angle, nematic phase appears at rather high temperature, and at low temperature region S_b decreases as temperature decreases while σ increases, that indicates that the nematic phase and smectic phases are uniaxial where the finite value of S_b is considered to come from the smallness of system size. On the other hand, in the large bend angle side, both of S and S_b are very small and comparable to each other, and a mono-domain of smectic layer is not achieved in the simulation. The order parameter σ is so small that a nematic–smectic phase transition temperature is not determined definitely.

Next, the relation of ordering to the molecular flexibility is studied by changing the strength of force constant for bend deformation, K_b. In

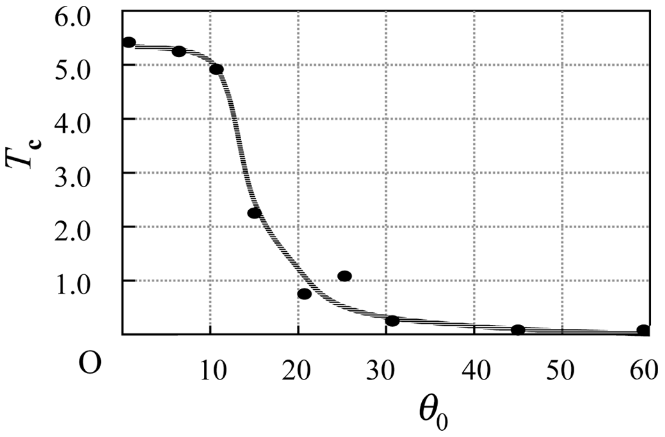


FIGURE 5 θ_0 dependence of clearing temperature T_c.

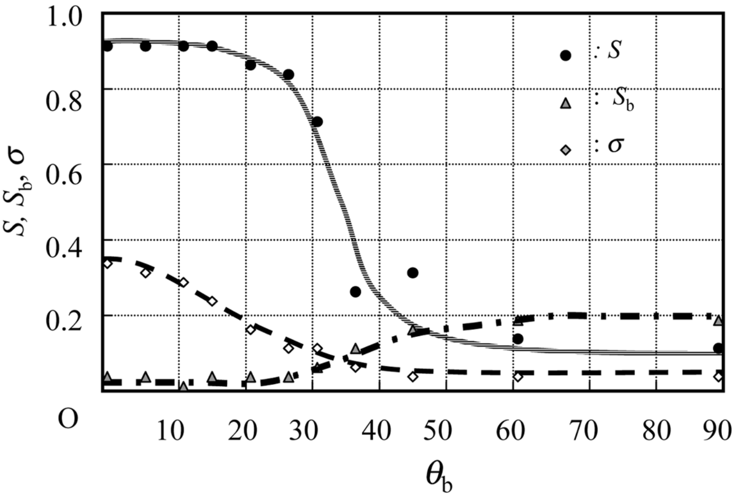


FIGURE 6 θ_0 dependences of S, S_b and sat enough low temperature.

Figure 7, the dependence of T_c on K_b is shown for the system with $\theta_0 = 15^\circ$, which shows a sigmoidal curve with inflection point near $K_b = 1$. As a natural result, the variance of θ centred at θ_0 becomes large as K_b becomes small, and in the limit of soft spring constant the clearing temperature is extremely small.

Lastly, the influence of molecular length together with molecular shape to the ordering is tested by the simulation at the systems of

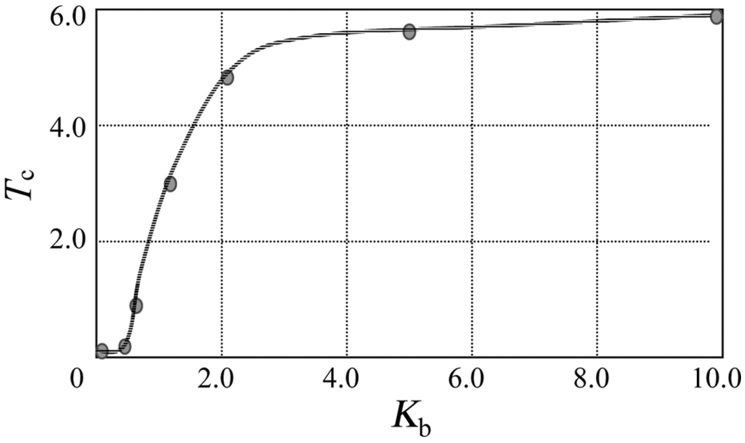


FIGURE 7 K_b dependence of clearing temperature T_c.

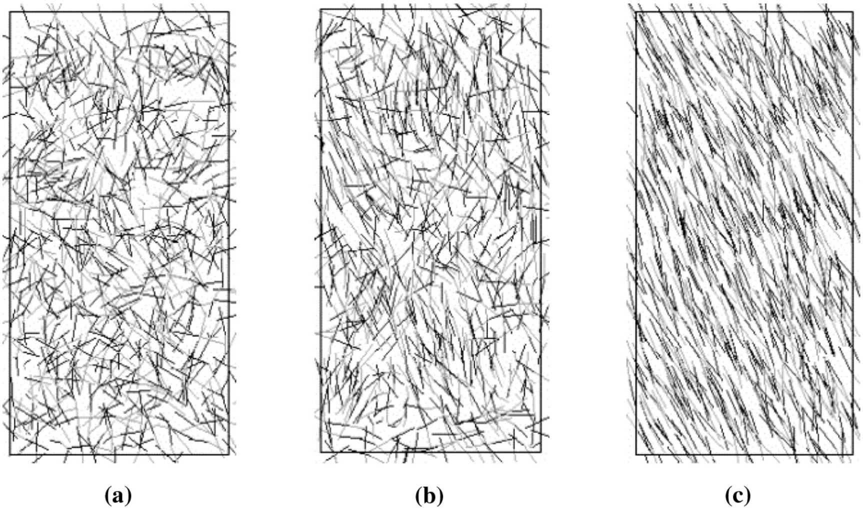


FIGURE 8 Snapshot of Model II with $\theta_0 = 15°$; (a) isotropic phase ($T = 8$), (b) nematic (or smectic) phase ($T = 1.5$), (c) smectic phase ($T = 0.5$).

Model II with $K_\mathrm{b} = 1$. Ordering process of Model II with $\theta_0 = 15°$ is shown in Figure 8; $S = 0.06$ at $T = 5$ in (a). We obtain $T_\mathrm{c} = 3.4$, which is compared with $T_\mathrm{c} = 2.4$ in Model I, and a profile of nematic phase (or smectic phase) at $T = 1.5$ is shown in (b) where $S = 0.75$ and $\sigma = 0.3$. The profile of smectic phase at $T = 0.5$ is shown in Figure

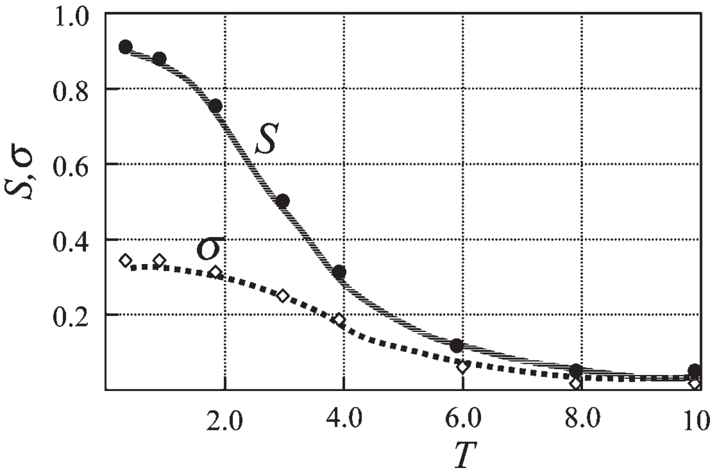


FIGURE 9 T-dependences of S and σ at Model II with $\theta_0 = 15°$.

8(c) with order, $S = 0.92$ and $\sigma = 0.34$. Temperature dependences of S and σ are shown in Figure 9, where both curves are observed to have each inflection point in the same temperature range. From this fact, we conclude that temperature range of nematic phase is very narrow, or isotropic phase changes to smectic phase directly.

To see this point clearly, the simulation at $\theta_0 = 30^\circ$ is also carried out. However, unfortunately the system exhibits similar ordering process to the one at $\theta_0 = 15^\circ$, even though the low transition temperature is observed. The system of Model III exhibits similar behaviour to the system of Model II, while a rate of ordering is slower and an achievement of ordered phase is incomplete.

SUMMARY

To elucidate the effect of molecular shape (bend angle θ_0 and molecular length) and molecular flexibility (bending force constant K_b) to the liquid crystalline ordering, NVT molecular dynamics simulation is carried out at the system of bent molecules which are dimers of two Gay-Berne particles with different lengths coupled by the harmonic spring at each end. The clearing temperature decreases as θ_0 increases, with sharp drop near $\theta_0 = 20^\circ$. The characteristics of ordering process is shown to change at an angle about $\theta_0 = 30^\circ$. In the system with small bend angle, the behaviour of the system is like the one occurring at a system of cylindrical molecules, where uniaxial nematic and smectic phases appear in the order as temperature decreases. On the other hand in the system with large bend, the ordering is the multi-domain phase. In each domain, the phase looks like biaxial smectic A phase with comparable values of S and S_b. Due to the smallness of smectic order parameter together with multi-domain, it is hard to estimate the nematic-smectic phase transition temperature.

The dependence of the ordering on the molecular flexibility is obtained by changing force constant of molecular bend deformation. The clearing temperature changes as sigmoidal curve with inflection point near the value $K_b = \varepsilon_0$. The variance of θ becomes large as the magnitude of K_b is reduced, and the nematic ordering is hardly observed in the soft limit of bend deformation.

By introducing different combinations of two Gay-Berne particles (Model II and Model III), the effect of molecular length and shape to the ordering is tested. In Model II where molecule is a type of banana-shaped, smectic ordering seems to occur almost simultaneously as the nematic order appears, where the ordering rate is very slow in comparison with the Model I. The ordering process in

Model III where the molecule is considered to be the shape of molecule of antiferroelectric smectics (though the permanent dipole is not taken into account, here), the behaviour of ordering is similar to the one at Model II, though the ordering motion is further slow and a certain final ordered state can not be achieved in the present simulation.

In the present system of dimer molecules with bend, a remarkable biaxiality is not observed, whereas ordering reveals a sign of biaxiality at quite low temperature at the system with large bend. In relation to the biaxial ordering of banana shaped molecular systems [11,12], detailed analysis such as a check of the order at each domain in multi-domain phase is required. At ferroelectric and antiferroelectric smectics [1–3], the length of constituent particle differs as Model III. To obtain a mono-domain structure at such system as Model III, some improvement or modification of simulation is required, which is an open question in the present study.

REFERENCES

[1] Nishiyama, I. & Goodby, J. W. (1992). *J. Mater. Chem.*, *2*, 1015.

[2] Miyachi, K., Matsushima, J., Takanishi, Y., Ishikawa, K., Takezoe, H., & Fukuda, A. (1995). *Phys. Rev. E*, *52*, R2153.

[3] Matsumoto, T., Fukuda, A., Johno, M., Motoyama, Y., Yui, T., Seomun, S. S., & Yamashita, M. (1999). *J. Mater. Chem.*, *9*, 2051.

[4] Bates, M. A. & Luckhurst, G. R. (1999). *Struct. Bond.*, *94*, 65 and article cited therein.

[5] Miyazaki, T. & Yamashita, M. (2002). *Ferroelectrics*, *276*, 147.

[6] Miyazaki, T. & Yamashita, M. (2004). *Mol. Cryst. Liq. Cryst.*, *413*, 2253.

[7] Miyazaki, T., Shigematsu, K., & Yamashita, M. (1998). *J. Phys. Soc. Jpn.*, *67*, 3477.

[8] Neal, M. P. & Parker, A. J. (2001). *Phys. Rev. E*, *63*, 11706.

[9] Sekine, T., Niori, T., Sone, M., Watanabe, J., Choi, S. W., Takanishi, Y., & Takezoe, H. (1997). *J. Appl. Phys.*, *36*, 6445.

[10] Thisayukta, J., Takezoe, H., & Watanabe, J. (2001). *J. Appl. Phys.*, *40*, 3277.

[11] Niori, T., Sekine, T., Watanabe, J., & Takezoe, H. (1996). *J. Mater. Chem.*, *6*, 1231.

[12] Macdonald, R., Kentischer, F., Warnic, P., & Heppke, G. (1998). *Phys. Rev. Lett.*, *81*, 4408.