Studies of Molecular Orientation for Ferrielectric Liquid Crystal by Phase Transitions

S. W. Kim[1], H. Choi[1], J. H. Song[1], J. H. Kim[2], S. Kumar[2], J. W. Choi[3], Y. B. Kim[3], and S. T. Shin[1]

[1]Department of Physics, Korea University, ChoongNam 339-800, Korea

[2]Department of Physics, Kent State University, Kent, Ohio 44242, USA

[3]Department of Chemistry, College of Science, Kon-Kuk University, Seoul 143-701, Korea

Abstract

We have studied the molecular orientation by the phase transitions of the chiral smectic liquid crystals, 4-(1-Trifluoromethyl-6-ethoxy-hexyloxycarbonlphenyl)-4-nonyloxybiphenyl-4-carbo-xylate (R-TFMEOHPNBC) to seek the original solution of the zig-zag defect using two different experimental techniques; optical system and x-ray scattering. The phase sequence is gamma ferroelectric (SmCγ *) → smectic A (SmA) → isotropic (I). Existence of two layer spacing at chiral smectic phase gives a possibility of the molecular orientation in two different tilt angles, θ_1 and θ_2, which are separated each other to the layer normal at a given temperature. The gamma ferroelectric-like phase is, first, discovered in the single compound.

Introduction

Since Dakezoe *et. al.*[1] discovered anti-ferroelectric liquid crystal (AFLC) in 1988, AFLCs have been a subject of intense investigations for application and basic research. Significant basic research has been done towards understanding their structure, thresholdless switching phenomena[2], electroclinic effect[3], and the existence of antiferroelectricity in achiral materials[4]. Owing to their unique properties, they are considered as prime candidates for thin-film transistor(TFT) LCD application which can be eligible for audio/video system.

In this paper, we have studied the molecular orientation and arrangement in the layer to obtain alignment technology to minimize the zig-zag defect for high contrast ratio, which is key and most important factor in success of AFLCD application. We report the results of phase transitions by x-ray scattering and induced polarization on electric field. We finally compare both results to study the molecular orientation and arrangement.

Experimental Details

The synthesis group of the Liquid Crystal Research Center at KonKuk univeristy headed by Y. B. Kim provided the necessary high-purity R-TFMEOHPNBC which is a single compound. The experiments for studying the phase transitions were performed on a 18-kW rotating anode source, and two-circle and four-circle goniometers with a pair of Ge(111) crystals used as monochromator and analyzer. The bulk sample aligned by slowly cooling from the isotropic phase in the presence of a ~3.0 kG magnetic field produced by a pair of rare-earth permanent magnets placed inside the oven. The temperature was kept stable to better than 10 mK. The experimental setup and other information is described elsewhere[5]. We used a method of pyro-current by triangular wave to obtain the spontaneous polarization(*Ps*). Schematic diagram of set/up for polarization were given in the Ref. 6. The temperature and data were controlled by computer using GPIB.

Results and Discussion

We have studied the molecular arrangement in bulk sample to originally solve the zig-zag defect caused by chevron structure. Smectic layer spacing, *d*, as a function of temperature is shown in Fig. 1. The behavior of *d* and phase change in the two smectic regions is in quantitative agreement with the other results obtained by using other techniques. The value of *d* obtained in a particular run didn't depend on sample history and on the time spent at any temperature. The temperature dependence of *d*, which increases abnormally with decreasing the temperature, is due to degree of bend of molecules on temperature. The tilt angle at the transition temperature from SmA to chiral smectic phase is ~9°. Two layer spacing appeared below ~64°C due to tilt angle or degree of bend of molecules. Solid circles represents main intensity which reverses at ~50°C and interval of two layer spacing slowly decreases with decreasing the temperature. Intensity at the chiral smectic phase is almost constant before appearing two layer spacing. At low temperature, change of intensity means that number of layer at peak position changes. It can be also explained that the growth of second peak indicates the increase of number of same layer which is relative with same tilt angle of molecules in layer.

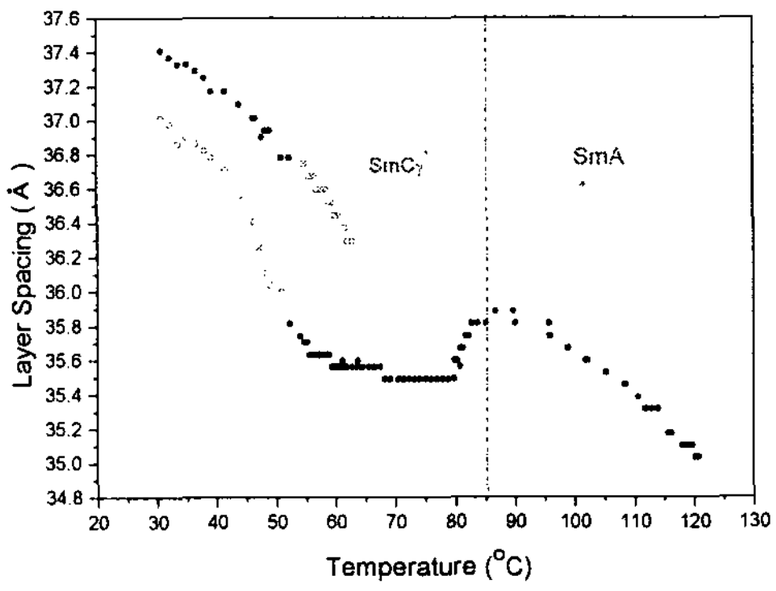

Figure 1. Smectic layer spacing as a function of temperature in phases. Solid and open circles represents main intensity, which reverses at ~50°C, and minor intensity, respectively.

Figure 2 shows two induced polarizations in one frame (positive electric field and negative electric field) understanding antiferroelectric phase below the SmA temperature. From the x-ray results, one layer spacing, which means the same tilt angle of

molecules to the layer, shows on the chiral smectic phase until the ~65°C from high temperature. The molecules arrange in the layer with the molecular long axis at the same tilt angle to the layer normal but in the opposite direction in two adjacent layers. In the above mentioned temperature region, the value of induced polarization is different in two cases when positive and negative fields applied. It is a clue to explain a ferrielectric phase or gamma ferroelectric phase (SmCγ *) which has the property of different number of molecular orientation, $n_1 > n_2$, on both side to the layer normal as shown in Fig. 3. Below the 65°C, the induced polarization gradually decreases with decreasing temperature, whose characteristic is a typical model for ferrielectric-like phase, due to equilibrium of free energy at the given temperature. The interval between two values of induced polarization obtained by negative and positive electric fields also decreases monotonically until 49℃ from ~60℃, but it is stable or higher below that temperature.

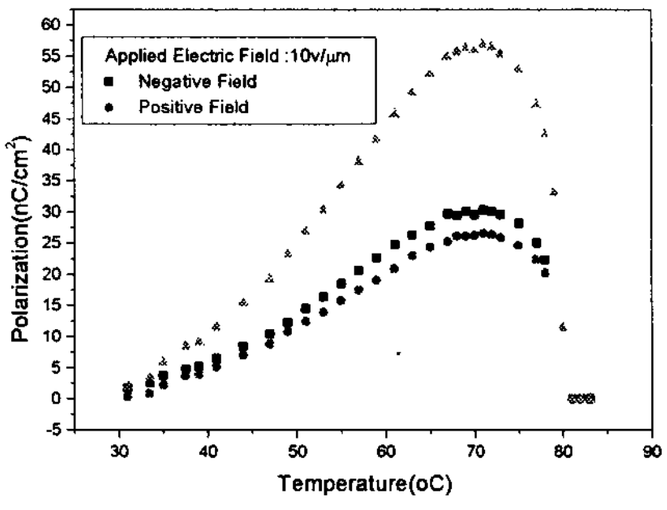

Figure 2. Induced polarization as function of a temperature at 10 V/m electric field. ● and ■ indicate the induced polarization obtained by the positive and negativeel ectricfield, respectively, and ▲ indicates the total induced polarization.

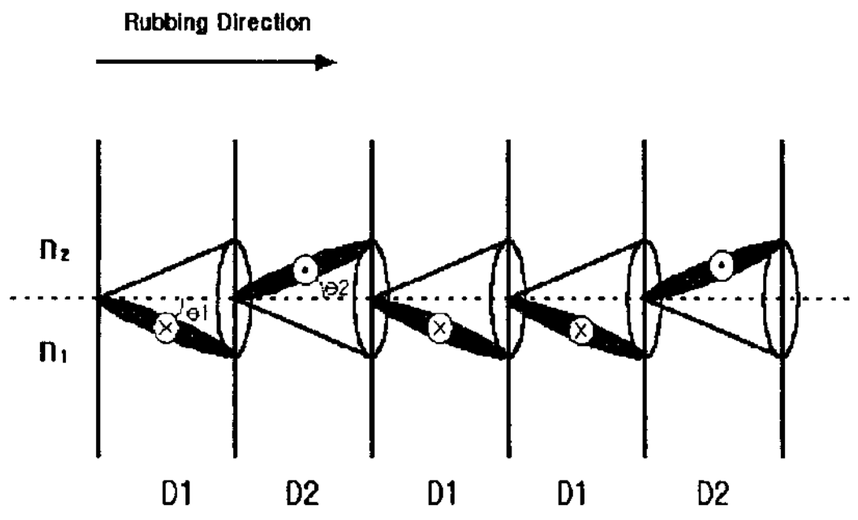

Figure 3. Modeling of ferrielectric phase ($n_1 > n_2$). ⊗ and ⊙ symbols indicate the direction of polarization at the above molecular orientation.

At 49°C, the peak intensities, which are ~3.5× 10^4 and ~2.5× 10^4 per 5e6 monitor counter at θ_1 and θ_2, respectively, are shown in Fig. 4. The larger peak is related with θ_1 which is mentioned above and smaller peak is related with θ_2. Two different intensities mean that number of layer spacing, n_1 and n_2, corresponding the θ_1 and θ_2 are different. What n_1 and n_2 are still not same below the 65°C can be explained the ferrielectric-like

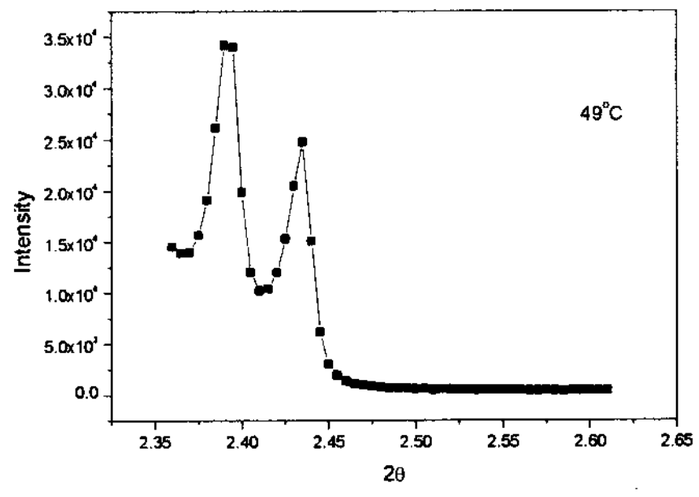

Figure 4. Intensity vs. 2θ.

phase. In general, average polarization is linearly proportional to tilt angle due to coupling interaction of dipole moment in adjacent layers. Relative value of polarization in the two cases depends on tilt angle and molecular reorientation at equilibrium state (minimization of free energy). Change of polarization by negative field is larger than change of polarization by positive field. A possibility can be followed from the above explanation. It is that the molecules oriented below (n_1) in Fig. 3 rearrange gradually on temperature with changing only tilt angle to θ_1 calculated by layer spacing D_1 according to x-ray results as shown in Fig. 1. The other molecules, (n_2), in Fig. 3 remain in the same orientation without changing the tilt angle, θ_2, if temperature is higher than 49°C. Here, θ_1 is smaller than θ_2 which depends on layer spacing, D_2. Below the 49°C, the n_2 molecules begin to tilt to θ_1 as function of temperature as shown the x-ray results. The relative polarization difference is not decreasing any more even though polarizations at negative and positive electric fields decrease, because the value of polarization with the positive field decreases more than its value with the negative field from tilting the n_2 molecules to θ_1.

Conclusions

We have presented the qualitative and quantitative analyses about molecular orientation and arrangement in layers by investigating the layer spacing and intensity obtained by x-ray scattering, and the induced polarization. Phase transition temperatures obtained by various experimental methods coincide each other. By the analyses of the x-ray result and the induced polarization, phase sequence of R-TFMEOHPNBC system is gamma ferroelectric (SmC*) → smectic A (SmA) → isotropic (I). Two tilt angles of molecular orientation to the layer normal at ~49°C, θ_1 and θ_2, are separated each other as shown in Fig. 3. The gamma ferroelectric-like phase is, first, discovered in the single compound.

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References

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