

Coherent director rotation and memory effects, and their dependence on the morphology of the constituent molecules in thiol-ene polymer stabilized ferroelectric liquid crystal system

Tong-Kun Lim* and Ji-Hoon Lee

Department of Physics, Korea University, Seoul 136-713, Korea
Phone: 82-2-3290-3094, E-mail: tongklim@korea.ac.kr

Abstract

We have studied the origin of coherent director rotation [CDR] as well as memory behavior in thiol-ene polymer stabilized ferroelectric liquid crystal [FLC]. The ene constituents are found to be always located at the inter-layer space and induce the coherent director rotation motion of liquid crystal molecule. On the other hand, the thiols are more intersticed between ferroelectric liquid crystal molecules at intra-layer as the thiol gets longer, and these intersticed thiols enhance the multistability and the resolution of memory state of FLCs.

1. Introduction

Recently polymer stabilized ferroelectric liquid crystal (PSFLC) system possessing attractive properties such as fast response, grayscale capability and good mechanical stability has been studied intensively for various applications [1-3]. In spite of these potentials, the exact relation between the specific morphology of constituent polymer and the resultant electro-optical properties of the system still remain open issues. This understanding of the system will undoubtedly be helpful from the viewpoint of physicochemical research and industrial application [4-6].

We have examined the origin of coherent director rotation as well as the multistable memory behaviors in connection with the specific morphology of the constituent polymer. The influence of orders in position as well as in orientation of ene and thiol molecules on the dynamic and the memory property were studied. Also the spontaneous polarization and the cone mode viscosity of samples have been examined to verify the detailed mechanism of electro-optical behavior.

2. Experiment

Commercially available bistable FLC FELIX-018/100 (Clariant) was mixed with thiol and ene in the weight percents of 90, 8, 2 wt%. Triallyl-1,3,5-triazine-2,4,6(1h,3h,5h)-trione (Aldrich) was used in all samples as ene monomer. Various linear molecules with different chain length such as 1,4-butane dithiol, 1,5-pentane dithiol, 1,6-hexane dithiol, 1,8-octane dithiol and 1,9-nonane dithiol (Aldrich) were used as thiol monomer.

A polyimide solution was spun on calcium fluoride (CaF₂) substrates which were already coated with indium-tin-oxide (ITO) and then the substrates were baked at 230 °C for 1 h. Rubbing directions were anti-parallel in each cell and the cell gap was 2 μm. The polarized infrared (IR) light absorption intensities of samples were measured by a Fourier transform infrared (FT-IR) spectrometer (FTS-7000, Bio-Rad). Electro-optical properties of samples were measured with similar set up as was used in the previous paper [1, 7]. Polymerizations were initiated via high pressure mercury (Hg) lamp with 40 mW intensity for 10 min.

Spontaneous polarization and cone mode viscosity was determined by measuring the current response to triangular wave applied to the sample as previously suggested [7-8].

3. Results and Discussion

Figure 1 (a) shows the optical birefringence of sample with 1,6-hexane dithiol that was polymerized at chiral smectic A (SmA*) phase at each electric field strength. It shows that the optical anisotropy remains almost unchanged, whereas the optic axis rotates as the field was strengthened. This means that the liquid crystal (LC) molecules rotate coherently at

each gray state as well as at saturated state. In addition, this sample shows *multistable memory* states after removal of the field, depending on the field strength before its removal. On the other hand, when polymerized at SmC* phase with same ene and thiol molecules, the sample shows *monostable memory* states, although it still shows coherent director rotation at dynamic mode.

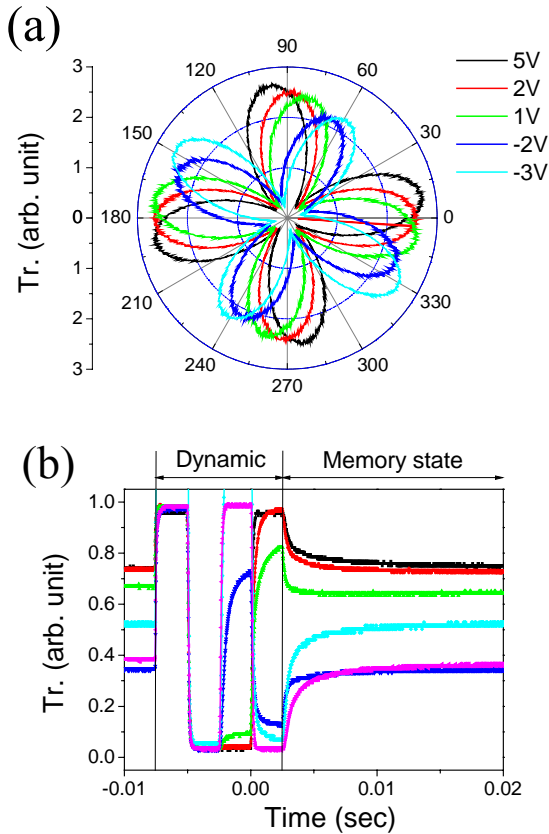


Figure 1: Optical birefringence of the sample with 1,6-hexane dithiol which was polymerized at SmA* phase (a) and memory property of that (b).

To verify the origin of distinct electro-optical properties between the two samples, we have examined the polarized IR absorption intensities of the constituent thiol and ene molecules for the C=C stretching of ene (1520 cm^{-1}) and for the S-H stretching of thiol (2570 cm^{-1}) at SmA* or at SmC* phase. For the sample with unpolymerized thiols and enes, the C=C stretch of ene molecules always absorb IR light most strongly in the layer direction regardless of the LC phase [Fig. 2 (a)]. These indicate that the

enes are in the inter-layer space with their orientation parallel to the inter-layer plane [Fig. 3]. For the S-H stretch of thiols, the direction of most strongly absorbed light is normal to the smectic layers at SmA* phase, while it is parallel with the smectic layers at SmC* phase [Fig. 2 (b)]. This indicates that the thiols are in the intra-layer space with their orientation parallel to FLC at SmA* phase [Fig. 3 (a)] while they are in the inter-layer space parallel to the inter-layer plane at SmC* phase [Fig. 3 (b)].

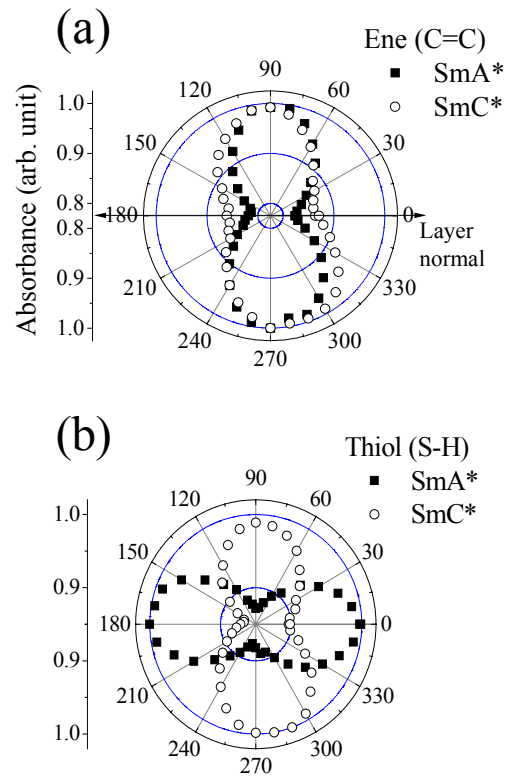


Figure 2: IR dichroism of the C=C stretch for the ene (a) and the S-H stretch for the thiol (b) at SmA* or SmC* phase before polymerization.

Next, we polymerized the thiols and enes in the sample either at SmA* phase (76°) or at SmC* phase (30°), and the IR dichroism was investigated [Fig. 3]. We found that the positions of polymerized thiols and enes do not change even when the phase of the sample was varied. Their positions were fixed to the same ones they took at the phase where they were polymerized [Fig. 3 (c), (d)].

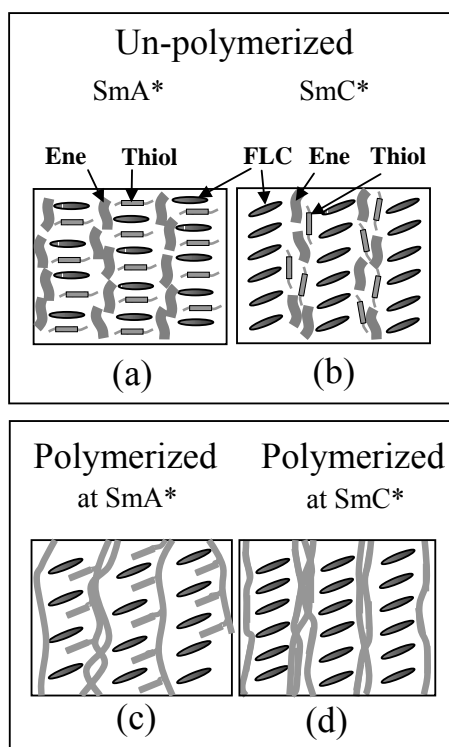


Figure 3: Schematics of orientation of constituent molecules before [(a) and (b)] and after polymerization [(c) and (d)].

The ene molecules seem to be always placed in the inter-layer space regardless of the polymerization phase and seem to induce coherent director rotation of LC. On the other hand, the thiol molecules seem to be intersticed between smectic layers only when it was polymerized at SmA* phase and in that case to enable the multistable memory effect.

To examine the dependence of memory behavior on the molecular length of thiol, we fabricated samples with thiol of different molecular length at different polymerization phase (SmA* or SmC*). Then the relation between the memory property and the dichroic ratio of thiol (defined as $\text{absorption}_{\text{layer normal direction}} / \text{absorption}_{\text{layer parallel direction}}$ at 2570cm^{-1}) as well as the resolution (defined as $(\text{Transmittance}_{\text{max}} - \text{Transmittance}_{\text{min}})_{\text{memory}} / (\text{Transmittance}_{\text{max}} - \text{Transmittance}_{\text{min}})_{\text{dynamic}}$) were examined.

The dichroic ratio of thiol shows strong correlation with the resolution as well as with the multistability of memory states [Fig. 4]. As the thiols are more intersticed into the smectic layers, the multistability and the resolution is enhanced. In

addition, as the thiol is lengthened, the dichroic ratio is increased.

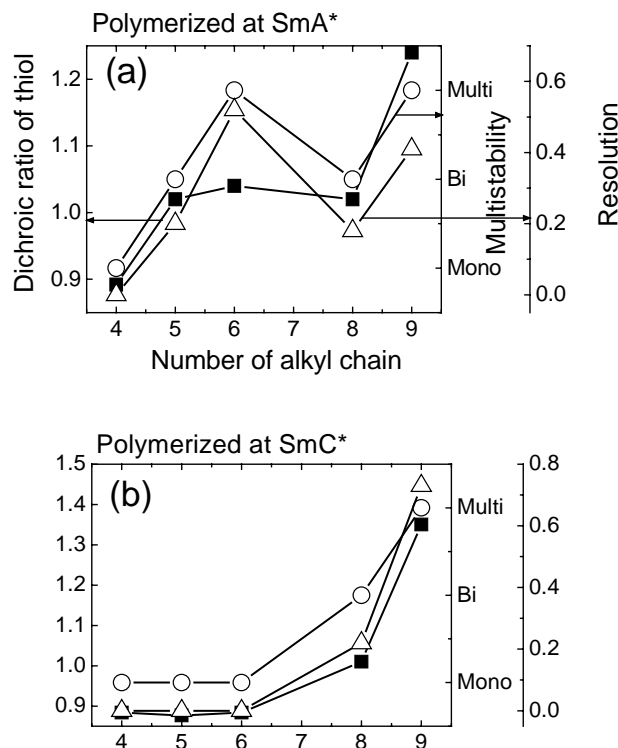


Figure 4: Dichroic ratio of thiol (■), multistability (○) and resolution (△) of memory states of the samples with different length of thiol which were polymerized at SmA phase (a) or SmC* phase (b), respectively.

We have asked whether the polymerization of thiol-ene are essential for the sample to show multistable memory behaviors. For the un-polymerized sample with 1,9-nonane dithiol, it shows monostable memory states although it has higher dichroic ratio. This means that the intersticed thiol must be attached to the ene in the inter-layer space to show multistable memory effect. We think that the intersticed thiols play analogous role as those pretitled molecules at the alignment layer surface of LC cell in fixing the LC molecules for the memory behavior with the orientation of thiols. On the otherhand, the CDR motion is observed always whether the polymerization is done or not.

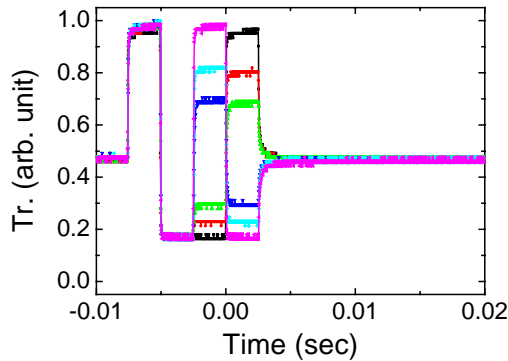


Figure 5: Memory property of the sample with 1,9-nonane dithiol before polymerization.

As the thiol lengthens, the spontaneous polarization decreases [□ and in Fig. 6 (a)]. To understand this behavior, we have measured cone angles of the samples and deduced the spontaneous polarization from them [△ and in Fig. 6(a)]. These data were compared with those from current response. They do well coincide to each other, so it can be concluded that the decrease of spontaneous polarization is due to the decrease of cone angle of FLC molecules.

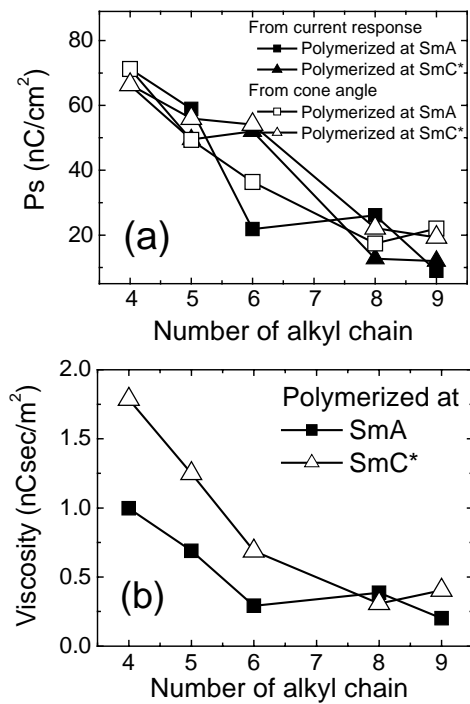


Figure 6: (a) spontaneous polarization deduced from current response or cone angle and (b) cone mode viscosity of the sample with different length of thiol which were polymerized at SmA or SmC* phase.

4. Conclusion

The ene constituents are always located at the inter-layer space and induce the coherent rotation motion of liquid crystal molecules. The thiols must be bound to enes for the sample to show memory behavior. They are more intersticed among the ferroelectric liquid crystal molecules at intra-layer as the thiol gets longer, and these enhance the multistability and the resolution of memory states. In addition, thiols must be bound to the ene through polymerization in order to show multistable memory states.

The cone mode viscosity was decreased as the thiol gets longer and this also seems to contribute higher multistability and resolution of memory states.

5. References

- [1] S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals* (Wiley, New York, 1999), pp. 57-91, 115-129, 325-400.
- [2] H. Furue, T. Miyama, Y. Iimura, H. Hasebe, H. Takatsu and S. Kobayashi, *Jpn. J. Appl. Phys.* **36**, 1517 (1997)
- [3] C. D. Hoke, J. F. Li, Y. H. Lin, L. C. Chien and P. J. Bos, *Liq. Cryst.* **27**, 359 (2000)
- [4] C. A. Guymon, E. N. Hoggan, N. A. Clark, T. P. Rieker, D. M. Walba and C. N. Bowman, *Science* **275**, 57 (1997)
- [5] H. Fujikake, K. Takizawa, H. Kikuchi, T. Fujii and M. Kawakita and T. Aida, *Jpn. J. Appl. Phys.* **36**, 6449 (1997)
- [6] J. Lub, D. J. Broer, M. E. M. Antonio and G. N. Mol, *Liq. Cryst.* **24**, 375 (1998)
- [7] J. H. Lee and T. K. Lim, *J. Appl. Phys.* **97**, 084907 (2005)
- [8] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **22**, L661 (1983)