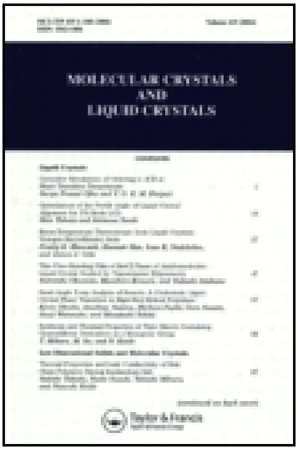

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Moojong Lim [a] , Byoungchoo Park [b] , Sang-Young Eom [a] & Sin-Doo Lee [a]

[a] Physics Department, Sogang University, C. P. O. Box 1142, Seoul, Korea

[b] Electronic Materials Research Lab., Institute for Advanced Engineering, C. P. O. Box 2849, Seoul, Korea

To cite this article: Moojong Lim , Byoungchoo Park , Sang-Young Eom & Sin-Doo Lee (1996): The Polar Order Coupling for Nonlinear Optical Molecules in a Ferroelectric Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 59-64

To link to this article: http://dx.doi.org/10.1080/10587259608040310

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 59–64
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THE POLAR ORDER COUPLING FOR NONLINEAR OPTICAL MOLECULES IN A FERROELECTRIC LIQUID CRYSTAL

MOOJONG LIM, BYOUNGCHOO PARK[†], SANG-YOUNG EOM,
and SIN-DOO LEE*
Physics Department, Sogang University, C. P. O. Box 1142, Seoul, Korea
[†]Electronic Materials Research Lab., Institute for Advanced Engineering,
C. P. O. Box 2849, Seoul, Korea

Abstract The polar order coupling effect in a ferroelectric liquid crystal (FLC) composite doped with nonlinear optical molecules has been studied by means of the second harmonic generation (SHG). The FLC composite is made up of a ferroelectric liquid crystal, SCE 13, doped with 5% of 4-dimethylamino-4'-nitro stilbenes (DANS) in weight. It is found that the SHG intensity from the doped DANS molecules is greatly enhanced by the polar order present in the FLC environment. Moreover, a delicate interplay between the orientational coupling and the polar one determines the molecular orientation of DANS with respect to the molecular director of the FLC.

INTRODUCTION

Recently, ferroelectric liquid crystals (FLCs) have been paid much attention from their promising applications in the area of displays. The development of FLCs for nonlinear optical (NLO) applications has been the subject of present research activities. In contrast to most non-crystalline phases, FLCs exhibit the second-order NLO processes because of the non-centrosymmetry. However, the NLO response of FLCs turned out to be relatively small compared to that of typical NLO materials.[1] Since the first observation of the second harmonic generation (SHG),[2] higher NLO active FLCs were designed.[3,4]

For improving the NLO properties, one approach is to combine the NLO functionality with ferroelectricity and liquid crystallinity. The other is to introduce high NLO activity into FLCs by doping proper NLO molecules. In the second case, the polar order coupling in the FLC environment will play a significant role in the alignment of the doped NLO molecules. In this work, we describe the concept behind the non-centrosymmetric macroscopic configuration in a FLC composite, and present results for the enhanced NLO properties by the dopant molecules. It is also discussed how the stable configuration for the dopant in the FLC environment will change with an external field.

EXPERIMENTAL

We used a commercial FLC mixture, SCE 13, obtained from British Drug House in this study. It has the ferroelectric, smectic C* phase between −20.0°C and 60.8°C. The molecular tilt ϕ_t and the spontaneous polarization P_s of SCE 13 is 22° and 27.8 nC/cm^2 at 20°C, respectively. The FLC composite was made up of SCE 13, doped with 5% of 4-dimethylamino-4'-nitro stilbenes (DANS) in weight. The measurements were made on a homogeneously aligned cell of 10 μm thick at an oblique incidence θ at room temperature. The SHG intensities were measured as a function of the azimuthal angle for rotation, ϕ, as shown in Fig. 1.

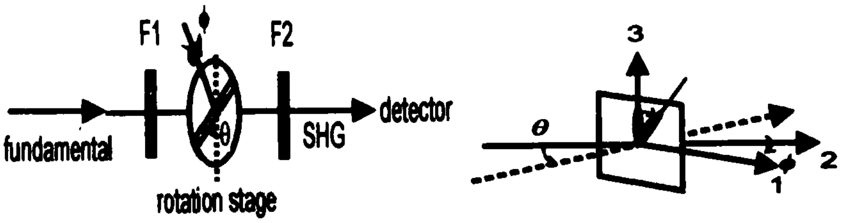

FIGURE 1 The experimental geometry; F1 and F2 are a visible filter and an IR cutoff one.

RESULTS AND DISCUSSION

By applying an external electric field along the 2-axis above a certain threshold (~ 5 V/μm), the polarization of the FLC becomes oriented along the field, and the FLC molecules lie in the 1-3 plane. In this configuration, the FLC has a C_2 symmetry with respect to the polarization direction. For the C_2 point group, the molecular orientation and the NLO coefficients can be directly determined from the angular dependence, ϕ and θ, of the SHG intensity profiles.

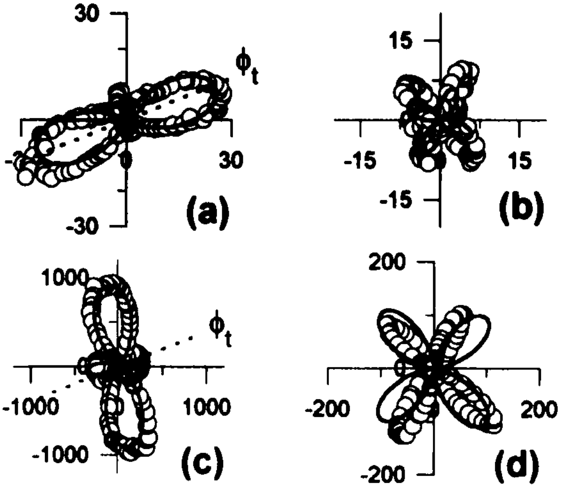

FIGURE 2 The SHG intensities for the p-polarized input at $\theta = 50°$: (a) p- and (b) s-polarized for SCE 13; (c) p- and (d) s-polarized for SCE 13/DANS.

Let us first describe the ϕ dependence of the SHG intensities in the presence of a dc electric field. The SHG intensities from SCE 13 and SCE 13/DANS were measured as a function of ϕ at $E = 10$ V/μm. As shown in Fig. 2, the remarkablly enhanced SHG intensities were observed for the SCE 13/DANS composite. From the ϕ dependence of the SHG intensities, the molecular tilt, ϕ_t, for both SCE 13 and SCE 13/DANS are estimated as 21.5° and 20.0°, respectively. The result agrees well with the literature value of 22.0°. Moreover, the magnitude of ϕ_t is nearly preserved on reversing the polarity of E.

We now examine the NLO coefficients, d_{ij}'s, determined from the ϕ dependence of the SHG intensity profiles. The measured values of d_{ij}'s for SCE 13 and SCE 13/DANS are collected in Table 1. A quartz plate was used as a reference[5] for evaluating the NLO coefficients from the SHG data.

Table 1 The measured values of d_{ij}'s at 10 V/μm (in unit of pm/V).

sample	d_{22}	d_{14}	d_{16}	d_{23}	ϕ_t
SCE 13	0.34	−0.004	0.002	−0.057	21.5°
SCE 13/DANS	2.5	6.5	−11.5	16.1	20.0°

For the SCE 13, d_{22} is the dominant tensor element. This means that the polar ordering of the FLC molecules plays a major role in the optical nonlinearity although FLCs with large P_s do not always show large NLO coefficients.[6] For the SCE 13 doped with DANS molecules, d_{ij}'s increase dramatically. Particularly, d_{16} for the SCE 13/DANS is about three orders of the magnitude larger than that for the SCE 13.

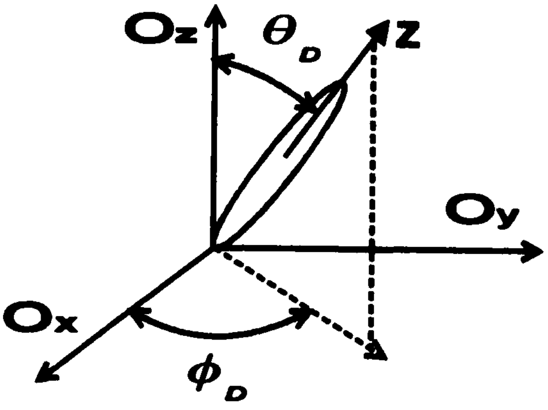

FIGURE 3 The molecular orientation of the DANS in the FLC environment. The optic axis and the polarization of the FLC are along O_z and O_y, respectively. For DANS, θ_D represents the polar angle, ϕ_D the azimuthal angle, and Z the optic axis.

In order to describe the polar order coupling effect for DANS in the FLC medium, we adopt a statistical thermodynamic approach to the induced alignment of DANS molecules by an external electric field. Assume that the DANS molecule is a one-dimensional chain with a dipole moment along the long axis, In an oriented gas model,[7] the macroscopic NLO coefficients associated with the hyperpolarizability β_{zzz} along the long axis (Z) of the DANS molecule can be written as

$$\begin{aligned} d_{22}^{DANS} &= N\beta_{zzz}F < \sin^3\theta_D >< \sin^3\phi_D > , \\ d_{23}^{DANS} &= N\beta_{zzz}F < \sin\theta_D \cos^2\theta_D >< \sin\phi_D > , \\ d_{16}^{DANS} &= N\beta_{zzz}F < \sin^2\theta_D \cos\theta_D >< \sin\phi_D \cos\phi_D > , \\ d_{14}^{DANS} &= N\beta_{zzz}F < \sin^3\theta_D >< \sin\phi_D \cos^2\phi_D > , \end{aligned} \tag{1}$$

where F is an appropriate local field factor,[1] and N is the number density of DANS. When the DANS molecules are oriented along the molecular director of the FLC (the 3-axis), $\theta_D \sim 0°$, and thus no contribution of DANS to the macroscopic NLO coefficients is expected. On the other hand, the maximum contribution is reached at $\theta_D \sim 90°$ and $\phi_D \sim 90°$ when the DANS molecules are along the field direction (the 2-axis).

By decoupling $d_{ij}^{DANS} = d_{ij}^{SCE13/DANS} - d_{ij}^{SCE13}$ to determine the degree of the enhanced NLO activity by the orientational ordering of the DANS molecules,

$$\begin{aligned} \theta_D &\sim \tan^{-1}[(d_{22}^{DANS} + d_{16}^{DANS})/d_{23}^{DANS}]^{1/2} , \\ \phi_D &\sim \tan^{-1}[d_{22}^{DANS}/d_{14}^{DANS}]^{1/2} . \end{aligned} \tag{2}$$

From the NLO coefficients of SCE 13 and SCE 13/DANS, θ_D and ϕ_D are estimated as 41.8° and 31.9°, respectively. In other words, the DANS molecules are oriented along a certain direction oblique to the molecular director of the FLC. This suggests that the delicate balance of intermolecular interactions between the DANS molecules and the FLC medium is an important factor for the NLO enhancement effect. Note that for some FLCs doped with dye molecules no enhanced SHG was observed.[8] Basically, the liquid crytalline potential acts as an orientational field for the DANS molecules along the 3-axis, and a dc electric field gives the polar field along the 2-axis.

CONCLUDING REMARKS

We have studied the second-order NLO properties of the FLC composite doped with NLO organic molecules. It is observed that doped NLO molecules tend to enhance the SHG intensity, measured as a function of the azimuthal angle for rotation. The absolute values of the NLO coefficients were determined from the SHG intensity profiles. Moreover, the microscopic orientation of the guest NLO molecules in the FLC medium was estimated from the NLO coefficients in a simple decoupled model. It is suggested that the degree of polar order coupling for the doped NLO molecules in the FLC environment plays a significant role in the enhanced NLO mechanism.

ACKNOWLEDGMENT

This work was supported in part by both KIST and KOSEF through RCDAMP at Pusan University.

REFERENCES

1. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers (Wiley, New York, 1991).
2. A. N. Vtyurin, V. P. Ermakov, B. I. Ostrovskii, and V. F. Shabanov, Krystallografiya, 26, 546 (1981).
3. D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and D. Doroski, Mol. Cryst. Liq. Cryst. 198, 51 (1991).
4. K. Schmitt, R. P. Herr, M. Schadt, J. Fünfschilling, R. Buchecker, X. H. Chen, and C. Benecke, Liq. Cryst. 14, 1735 (1993).
5. J. Jerphagnon and S. Kurtz, Phys. Rev. B 1, 1739 (1970).
6. M. Ozaki, M. Utsumi, T. Gotou, Y. Morita, K. Daido, Y. Sadohara, and K. Yoshino, Ferroelectrics, 121, 259 (1991).
7. J. Zyss and J. L. Oudar, Phys. Rev. A 26, 2028 (1982).
8. M. Ozaki, M. Utsumi, Y. Uchiyama, and K. Yoshino, Ferroelectrics, 148, 337 (1993).