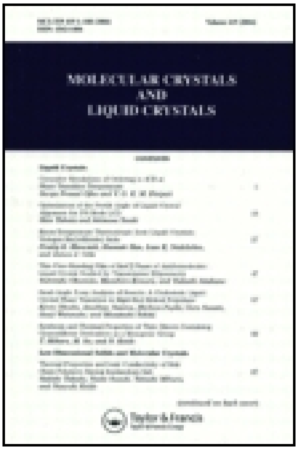


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferroelectricity in Liquid Crystals

Hideo Takezoe [a] & Junji Watanabe [b]

[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

[b] Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

Version of record first published: 24 Sep 2006

To cite this article: Hideo Takezoe & Junji Watanabe (1999): Ferroelectricity in Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 328:1, 325-332

To link to this article: http://dx.doi.org/10.1080/10587259908026074

Mol. Cryst. Liq. Cryst., 1999, Vol. 328, pp. 325-332
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Ferroelectricity in Liquid Crystals

HIDEO TAKEZOE[a] and JUNJI WATANABE[b]

[a]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152–8552, Japan and* [b]*Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152–8552, Japan*

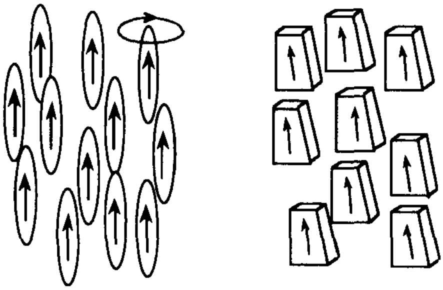
After summarizing ferroelectric and antiferroelectric liquid crystals (LCs) in liquid crystals so far discovered, two materials exhibiting a proper ferroelectricity are reported; (1) polar order in nematic LC of aromatic polyesters and (2) ferroelectric switching in a lyotropic liquid crystal of polypeptide. In the polypeptide LC, strong second-harmonic generation (SHG) was observed by applying an electric field, and the phase of the SH field was reversed by reversing the field, indicating the ferroelectric switching of the nonlinear polarization. SHG was also observed in the unperturbed helical state when the incident light with the wavelength the same as the helical pitch is passed through along the helical axis. In the aromatic polyester LC, SHG arises when the degree of polymerization is larger than 20. It is proposed that these polar organization originates from the dipole-dipole interaction, namely the proper ferroelectricity.

Keywords: polypeptide; second-harmonic generation; ferroelectric liquid crystal; proper ferroelectricity; helical structure; SHG interferometry; distributed feedback cavity

INTRODUCTION

For the materials to be ferroelectric, the system must be noncentrosymmetric. Then, a polarization could exist in the system. If the polarization can be reversed by changing the polarity of the electric field with a single hysteresis, the system is called ferroelectric. For antiferroelectricity, the positive and negative polarizations are located alternatively. By applying an electric field, the alternate polarization state (antiferroelectric state) changes to the ferroelectric states with positive and negative polarizations. The switching is associated with a double-hysteresis loop.

As well known, the first ferroelectric liquid crystal (LC) was realized in the smectic C (SmC) phase by introducing a chiral carbon to reduce the symmetry, *i. e.*, SmC*[1]. However, the introduction of chirality is not a necessary condition to realize ferroelectricity in LCs. Ferroelectricity possibly arises, if one can construct systems with C_n or C_{nv} symmetry. Some realistic molecular orientations are shown in Fig. 1; (a) polar uniaxial nematic LC with $C_{\infty v}$ symmetry, (2) polar biaxial nematic LC with C_{1v} (C_s) symmetry, (3) polar uniaxial SmA LC with $C_{\infty v}$ symmetry and (4) polar biaxial Sm LC with C_{2v} symmetry. For rod-like molecules, the structures (a) and (c) do not usually appear, since the head-and-tail equivalent


(a) Polar Nematic LC $C_{\infty v}$ (b) Polar Biaxial Nematic LC C_s

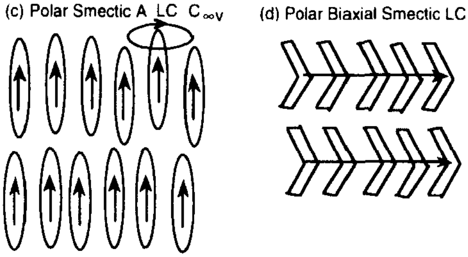

(c) Polar Smectic A LC $C_{\infty v}$ (d) Polar Biaxial Smectic LC C_{2v}

FIGURE 1. Possible molecular orientation for ferroelectric liquid crystals formed by achiral molecules.

arrangement is thermodynamically preferred. The difficulty in constructing the structures (a)~(d) had prevented us from realizing such ferroelectricity until just recently.

Recently Tournilhac *et al.*[2] reported the piezoelectricity in SmA, in which molecules forms a polar structure shown in Fig. 1(c) as a result of the segregation of molecular units into homogeneous microdomains due to the polyphilic interaction. More distinct ferroelectricity was reported by Niori *et al.*[3] in bent-shaped molecular systems. The molecular orientation is essentially the same as that shown in Fig. 1(d), though a molecular tilting model and an antiferroelectric structure were proposed[4]. Namely, the polar ordering is caused by closely packing the bent-shaped molecules. Untilted antiferroelectric LC was also discovered recently[5]. Thus, ferroelectricity in all the examples mentioned above originates from particular interactions but is not caused by the dipole-dipole interaction; that is improper ferroelectricity.

We have already reported the polar ordering in a nematic LC of aromatic polyesters[6-8]. In this system, the polar ordering seems to occur by the dipole-dipole interaction. In this sense, this may be the first example of the proper ferroelectricity in LCs. However, because of high viscosity, the electric-field induced ferroelectric switching has not been observed. Recently, we found that the lyotropic cholesteric phase of polypeptide, *i. e.*, poly(γ-benzyl-L-glutamate-co-γ-methyl L-glutamate) (PBMLG) in benzyl alcohol is in fact a ferroelectric cholesteric phase[9]. This is the first proper ferroelectricity in liquid crystals. In the following, some experimental observations suggesting proper ferroelectricity in polyester LC and polypeptide LC will be reported.

EXPERIMENTAL

Two samples were used; (1) aromatic copolyester that comprises 4-hydroxy benzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA), as shown in Fig. 2, and (2) PBMLG, which exhibits the lyotropic liquid crystal in benzyl alcohol. It is characteristic that both molecules are of rigid rod-like and have a large dipole moment along the molecular long axis. The cell preparation method was described previously.[6,9]

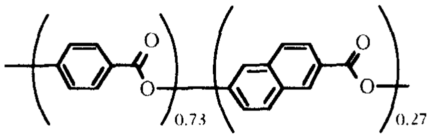


FIGURE 2. Aromatic copolyester used.

The SHG measurements were made using a Q-switched Nd:YAG laser (1.06 μm), as described.[6,9] SHG interferometry was also conducted. As shown in Fig. 3, a crystal quartz plate was inserted on the optical path. Then, SH waves were generated both from the quartz plate and the sample and interfered to each other. A fused silica plate was located between the quartz plate and the sample cell, and was rotated about the axis parallel to the fused silica plate and perpendicular to the optical path, producing a relative phase change between SH waves from the two sources because of a frequency dispersion of the refractive index of the fused silica plate. In this way, we observed interference fringes.

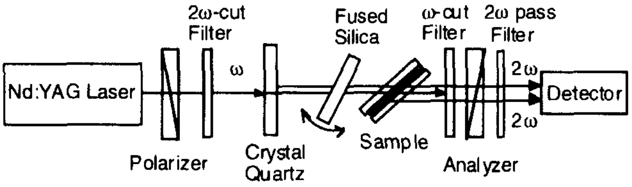


FIGURE 3. Optical geometry of SHG interferometry experiment.

In order to study the distributed feedback (DFB) cavity effect[10-12] in helical state of PBMLG, SHG was measured using normally incident two-counter propagating fundamental waves of a Nd:YAG laser (wavelength 1.064 μm), as illustrated in Fig. 4.

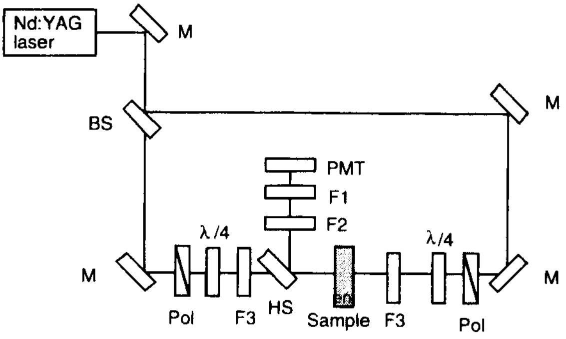


FIGURE 4 Optical geometry for observing DFB cavity effect.

RESULTS AND DISCUSSION

Figure 5 shows the SHG intensity as a function of degree of polymerization of aromatic polyester[13]. At about a degree of polymerization of 20, SHG starts to arise spontaneously. This result strongly suggests that the polar ordering originates from the increasing dipole-dipole interaction.

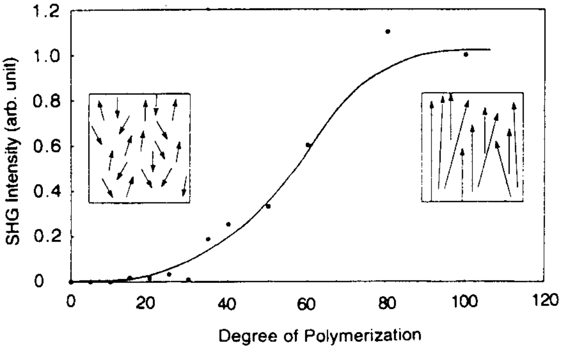


FIGURE 5 SHG intensity as a function of degree of polymerization in the main chain aromatic polyester LC.

In PBMLG, strong SHG was observed by applying an electric field[9]. In order to confirm the ferroelectric switching, an SHG interferometry experiment was made. The result is shown in Fig. 6. It is clear that an interference fringe is seen and the phase of the fringe is just reversed by changing the polarity of the field.

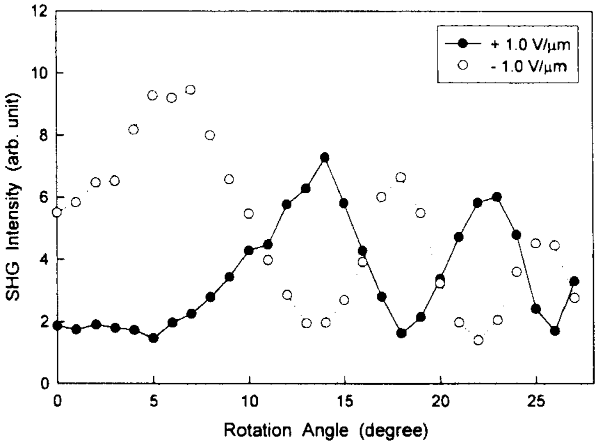


FIGURE 6. SHG interference fringes observed under ±1 V/μm. Note that the fringes are just reversed by the polarity change.

To further confirm the polar structure in the unperturbed helical state, SHG was observed without applying a field. The method used was the DFB cavity effect observed in a ferroelectric LC[10-12]. The sample used was a PBMLG film prepared to give a gradient of the helical pitch. The SHG intensity was observed by translating the film along the direction of the pitch gradient using the optical geometry shown in Fig. 4. The result shown in Fig. 7 clearly exhibits a peak at a certain position. The transmittance of the SH light of the Nd:YAG laser (532 nm) is also shown in Fig. 7 as a function of sample position. The transmittance exhibits a dip at the same position where SHG shows the peak. This dip is due to the selective reflection and assures that an enhanced SHG is observed when the

SH light wavelength coincides with the optical pitch, that is the DFB effect. The observation of the DFB cavity effect unambiguously indicates that a plane perpendicular to the helical axis is polar. Thus, it is concluded that PBMLG has a ferroelectric cholesteric structure. The experiment in the LC phase is in progress.

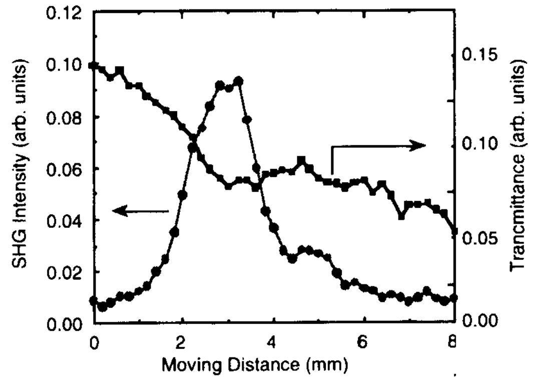


FIGURE 7 SHG intensity as a function of sample position, along which the helical pitch changes. Transmittance of 532 nm light also exhibits a dip at the same position as that showing the SHG maximum.

Ferroelectric nematic phase has been theoretically predicted[14,15]. Trentjev *et al.*[14] suggested that ferroelectricity is more likely to occur in nematic polymer with directed polar segments. The polypeptide system is just an ideal system from this viewpoint. Lee and Lee[15] drew several phase diagrams as a function of scaled dipolar strength, density and pressure, predicting the nematic-ferronematic phase transition. The present systems, *i. e.*, polypeptide and aromatic polyester, provide with the first examples of the proper ferroelectricity theoretically predicted.

CONCLUSION

After summarizing ferroelectric liquid crystals in liquid crystals, some experimental results suggesting the first proper ferroelectricity were presented; *i. e.*, polar nematic in aromatic polyester by the spontaneous SHG at higher degrees of polymerization than 20 and ferroelectric cholesteric in polypeptide by the SHG interferometry and the SHG-DFB effect.

Acknowledgment

We acknowledge Mr. Y. Q. Liu for his experiment of aromatic polyester. We also thank Dr. B. Park and Mr. D.-H. Chung for obtaining the data of Fig. 7, the details of which will be reported soon.

References

[1] R.B. Meyer, L. Liebert, L. Strzelecki and P.Keller, *J. Phys. (France)*, **36,** L69 (1975).

[2] F. Tournilhac, L.M. Blinov, J. Simon and S.V. Yablonsky, *Nature*, **359,** 621 (1992).

[3] T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H.Takezoe, *J. Mater. Chem.*, **6,** 1231 (1996).

[4] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Korblova and D.M. Walba, *Science*, **278,** 1924 (1997).

[5] J. Watanabe, T. Niori, S.-W. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, **37,** L401 (1998).

[6] T. Watanabe, S. Miyata, T. Furukawa, H. Takezoe, T. Nishi, M. Sone, A. Migita and J. Watanabe, *Jpn. J. Appl. Phys.*, **35,** L505 (1996).

[7] T. Furukawa, K. Ishikawa, H. Takezoe, A. Fukuda, T. Watanabe, S. Miyata, T. Nishi, M. Sone and J. Watanabe, *Nonlinear Optics*, **15,** 167 (1996).

[8] T. Furukawa, H. Takezoe, T. Nishi, T. Mitsukuchi, A. Migita, J. Watanabe, T. Watanabe and S. Miyata, *Mol. Cryst. Liq. Cryst.*, **299,** 105 (1997).

[9] B. Park, Y. Kinoshita, H. Takezoe and J. Watanabe, *Jpn. J. Appl. Phys.*, **37,** L136 (1998).

[10] J-G. Yoo, S-W. Choi, H. Hoshi, K. Ishikawa, H. Takezoe and M. Schadt, *Jpn. J. Appl. Phys.*, **36,** L1168 (1997).

[11] M. Copic and I. Drevensek-Olenik, *Liq. Cryst.*, **21,** 233 (1996).

[12] I. Drevensek-Olenik and M. Copic, *Phys. Rev.*, **E56,** 581 (1997).

[13] Y.Q. Liu, *Master Thesis* (Tokyo Institute of Technology, 1998).

[14] E.M. Terentjev, M.A. Osipov and T.J. Sluckin, *J. Phys. A: Math. Gen.*, **27,** 7047 (1994).

[15] J. Lee and S.-D. Lee, *Mol. Cryst. Liq. Cryst.* **254,** 395 (1994).