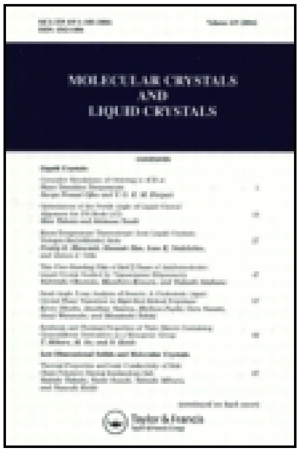


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Nonlinear Optical Properties of the Main-Chain Type Liquid Crystalline Polymers and Electric Fields

Tadahiro Asada [a]

[a] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, 606, Japan

To cite this article: Tadahiro Asada (1998): Nonlinear Optical Properties of the Main-Chain Type Liquid Crystalline Polymers and Electric Fields, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 318:1, 39-58

To link to this article: http://dx.doi.org/10.1080/10587259808045374

Mol. Cryst. Liq. Cryst., Vol. 318, pp. 39–57
Reprints available directly from the publisher
Photocopying permitted by license only

Nonlinear Optical Properties of the Main-Chain Type Liquid Crystalline Polymers and Electric Fields

TADAHIRO ASADA
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, 606 Japan

The second harmonic generations (SHG) of liquid crystalline main-chain type polymers were investigated. The sample polymers are copolymers of 2-hydroxy-6-naphthoic acid (HNA) with 4-hydroxy-benzoic acid (PHB), in various composition ratios. The SHG of the film samples was greatly affected not only by the polymerization conditions, but also by preparation conditions of the films. SHGs for the samples processed by mechanical stretching and for electrically poled samples were compared. The nonlinear optical coefficients d_{exp} evaluated by Maker Fringe method of the electrically poled samples are 2-3 times larger than that of the mechanically oriented sample whose d_{exp} is about 5pm/V. Trials of Quasi-Phase Matching of periodically inverted-polarized films show very effective to improve SH efficiency. A method that can control SH efficiency by application of electric field is proposed.

Keywords: nonlinear optics; second harmonic generation; liquid crystalline main-chain polymer; mechanically oriented sample; electrically oriented sample; Maker Fringe Method

INTRODUCTION

Nonlinear optics (NLO) is currently at the forefront of research because it is the key hard ware technology for optical communication, signal processing and optical computing. Optically nonlinear polymers are new kinds of the NLO materials, which have recently been the focus of the intensive fundamentally and applied research by academic, industrial and governmental laboratories[1-3]. The reasons for this include the excellent thin films obtained from polymers, their superior mechanical properties, especially, their tailorability through chemical synthesis and processing[4-5]. Usually, the NLO polymers are divided into three kinds, (1) the guest-host NLO polymers, (2) the side-chain NLO polymers and (3) the main-chain NLO polymers. The first one can be easily obtained by blending the NLO organic materials with transparent polymers. The second one is to combine the NLO moiety to the main-chain of the polymers as the side-chain by chemical reaction or polymerization procedure. However, in these two, there exists a problem of orientational relaxation of NLO moiety[6-8]. The last one may be divided into two categories: the one is the NLO moiety combined in the main-chain and the other is the main-chain itself showing large NLO properties.

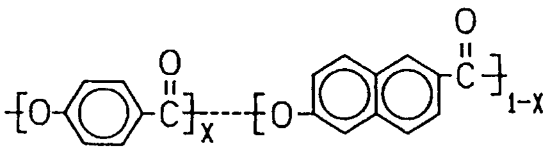
It has been shown that in order to generate second harmonic, inversion symmetry must be broken on a molecular scale, but also on a solid structure. Some liquid crystal polymers may exhibit very large optical nonlinearities[9]. The molecular structure of the liquid crystal polymers is noncentrosymmetry, and the molecules are easily oriented to get solid structure with broken symmetry, when they are processed in the liquid crystalline state. The advantages to use liquid crystalline main-chain polymer will be; (1) accumulation of the effect of individual units due to head to tail bonding, (2) spontaneous orientation of chain molecules, and (3) high stability (mechanically and against temperature, etc.). Therefore, a study has been carried out to improve the second harmonic generation (SHG) of liquid crystalline main-chain polymers[10].

In this work, the SHG of the liquid crystalline main-chain polymers was investigated. It was found that the SHG of the films was greatly affected by the processing conditions of the films. A new special alignment technique has been developed to get the SHG of the films double than that of the one formed usually in a T-die extrusion, etc. The largest second order nonlinear optical coefficient (d_{33}) of the film is above $10 \times d_{11}$ that of the quartz. Besides, the poling effects during the sample preparations will be introduced and be compared with mechanical orientation effects. Finally, some trials of Quasi-Phase Matching (QPM) by making periodically inverted-polarization thin films will be introduced.

EXPERIMENTAL

Materials

The chemical structure of the copolymer synthesized is as follows:



[PHB-HNA $]_N$

Copolymers of PHB and HNA in various molar ratios were prepared: 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90. The preparation of these wholly aromatic copolyesters requires a melt condensation of 6-acetoxy-2-napthoic acid with 4-acetoxy benzoic acid at high temperatures (Ca. 350°C) in N_2 atmosphere. The samples with a degree of polymerization (DP) around 30 were selected and used. The DP was evaluated by the ^{1}HNMR end-group method.

The film of the sample was processed in various conditions, such as heating roller extension (HR-3) and instant two-opposite way extension method (a new technique developed by us). These film samples obtained by mechanical processing, are called mechanically oriented samples, hereafter, and the orientation direction of the molecules is parallel to the machine direction.

The procedure for electrically oriented samples will be described later.

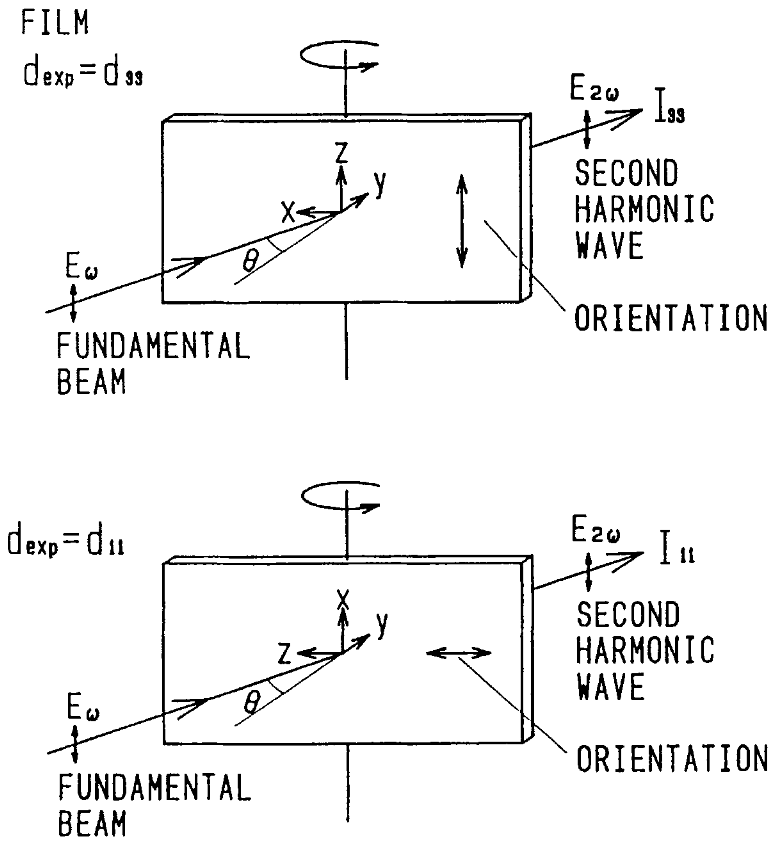


FIGURE 1 The Geometry for the measurements of Maker Fringe Method and NLO coefficients to be obtained.

Measurements

Nonlinear optical (NLO) properties

The SHG of the samples was evaluated by both the powder method (for as polymerized samples) and Maker Fringe Method[11]. The Nd: YAG laser (Spectron, SL401) was used as the light source (wavelength=1064nm). The experimental apparatus for SHG measurements has been described previously[10]. The second harmonic NLO coefficient d_{33} of the films was evaluated by the Maker Fringe Method[11], compared with standard Y-cut quartz d_{11}. The geometry of the Maker Fringe measurements are shown in Fig. 1. In case it was difficult to use Maker Fringe Method to obtain d_{33} or d_{exp} for a film sample was evaluated by using Yariv's Equation[12].

X-ray diffraction

X-ray diffraction experiments were performed using Rigaku X-ray generators. For the measurements of the intensity-angle curve, a Model Rad-B was used with Cu Kα radiation. For the diffraction patterns, two dimensional time sharing measurements and data analysis system of X-ray diagram (Rigaku Model DIP 220) were used.

Electro-optical properties

To determine the conditions by which an electrically oriented (poled) sample of high efficient NLO properties is obtained, the electro-optical properties of the copolyester-samples were examined, beforehand. The apparatus and methods used for this purpose have been reported previously[13]. The cell used had two parallel glass plates coated inside with conductive thin layers (In_2O_3) separated

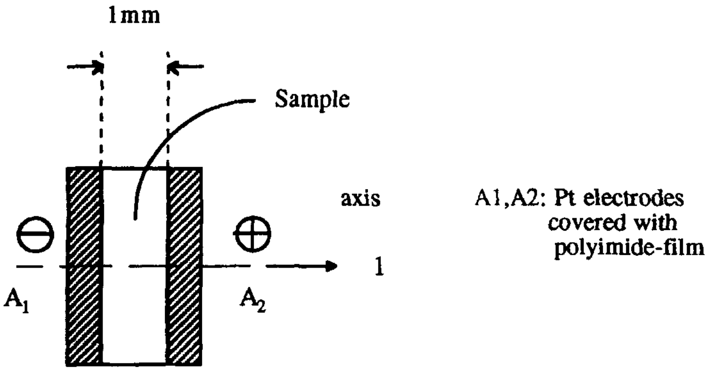


FIGURE 2 Transversely-applied electric field cell.

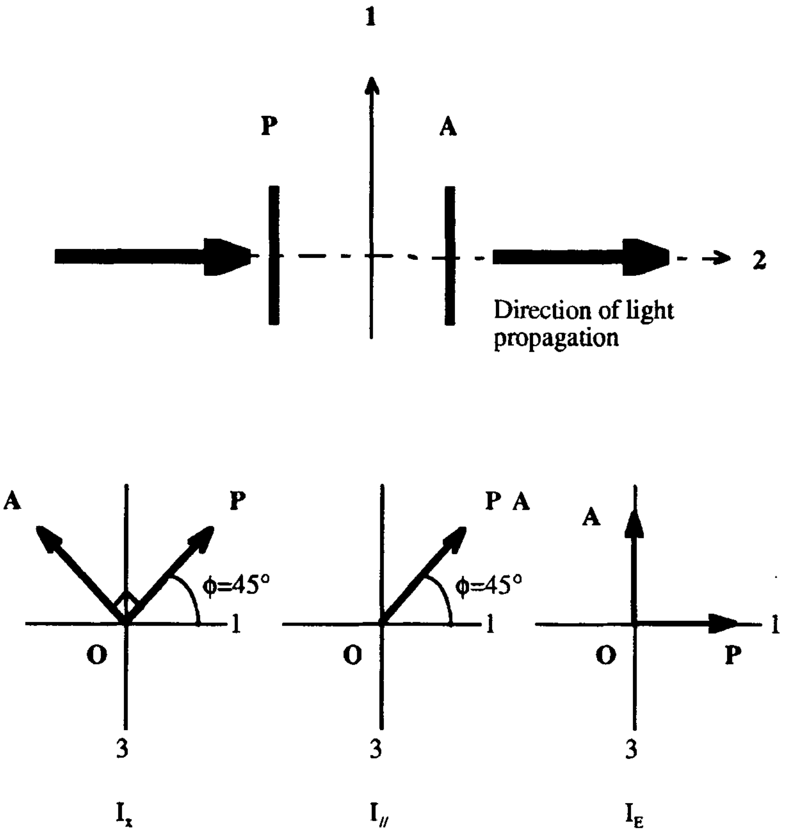


FIGURE 3 Optical geometry.
OP: transmission axis of polarizer
OA: transmission axis of analyzer

by a sheet of mica (thickness=20-25μm) with a square window 3×3mm in width. The direction of the electric field is perpendicular to the plates of the cell coinciding with that of light propagation.

Under an appropriate electric field, the molecules were oriented almost homeotropically and the view became dark (crossed polarizers system). A large homeotropic monodomain texture appeared. In this case (Case E-1), the orientation direction of the molecules is perpendicular to the film surface. For comparison, electric field horizontally (transversely) applied cells (transverse cells) were also used (as shown in Fig.2, Case E-2). In this case, I_x and $I_{//}$ were measured right after application or cessation of voltage. Optical Geometry is shown in Fig. 3. From the changes of I_x and $I_{//}$, the changes of optical retardation (birefringence × thickness) can be obtained by Eq. (1) during the application or after cessation of voltage[13]. In this case, film, in which homogeneous orientation of molecules was achieved, was obtained. These film samples are called electrically oriented (E-2, transverse) samples, hereafter. The achieved oriented-structure was fixed by instant quenching maintaining the applied DC voltage, that is, the whole cell system was put in room temperature instantly at the same time the heaters were switched off.

$$\left.\begin{aligned} I_x &= K\sin^2(\pi\Gamma/\lambda) \\ I_{//} &= K[1-\sin^2(\pi\Gamma/\lambda)] \end{aligned}\right\} \qquad (1)$$

where Γ and λ are the optical retardation and the wavelength of the light, respectively. K is a coefficient that is unity when there is no absorption or scattering.

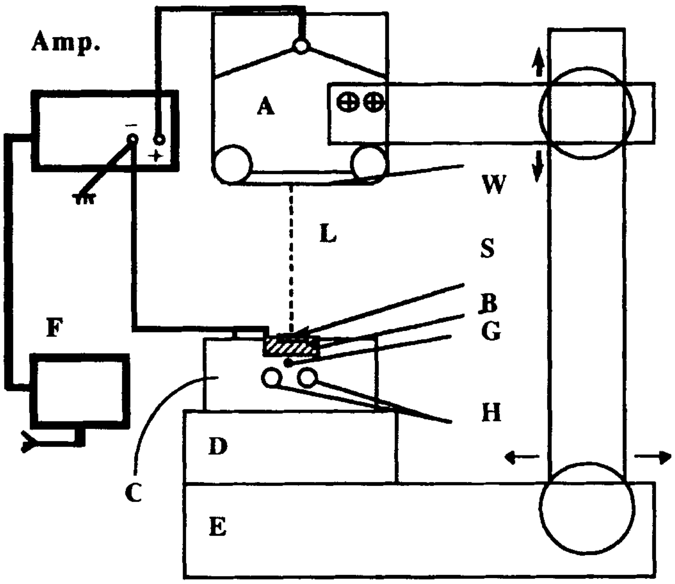


FIGURE 4 Schematic diagram for corona polling apparatus.
A: Ceramic block B: Conductive coated glass plate C: Heating block
D: Insulator E: Base F: Function generator G: Temperature sensor for temperature controller H: Heaters Amp: DC Amplifier
W: Tungsten wire(+)

Corona poling

The schematic diagram for corona poling apparatus is shown in Fig.4. A traveling microscope was modified to use as an adjustable electrode for corona poling, substituting microscope parts with electrode parts. A 2cm length tungsten wire was used as the plus electrode.

The sample prepared by corona poling will be noted as E-3. The applied voltage, time, and temperature will be described for individual specimen. 8kV, 18mm (between electrodes), at the liquid crystalline temperature 290°C, and 1 hour (application time) were most commonly used.

TABLE I. Films prepared by poling in the L.C. Temperature.

Sample Code	Application of DC - electric field	Alignment
E-1	Sandwich cell type	⊥ to film surface
E-2	Transverse cell type	// to film surface
E-3	Corona-poling	⊥ to film surface

RESULTS AND DISCUSSIONS

Accumulating Effect of Individual Unite

Calculation of hyperpololarizability (β)

The SHG of the copolyesters, for example PHB:HNA (60:40), is as large as that of methyl-nitroaniline (MNA), when compared with the so called powder method (Scattering SHG light intensities from the powder samples are compared). The large SHG of this copolyesters is not obvious from the chemical structure. However, the large SHG is evident when we calculate the hyperpolarizability (β) of some model compounds and take into account the fact that the sample is made of a polymer, that is, more than 20 individual units are linearly united by primary bonds, in a head-to-tail manner. Consequently, the additivity of hyperpolarizability (β) can be expected for such a system. Some examples of calculation by the molecular simulation method for the model compounds of this kind of polymer will be shown. The calculation procedure is as follows: (1) A molecule is constructed by the component moieties. (2) being optimized by using MNDO Parametric Method 3 (proposed by James J. P. Stewart[15]). (3) β is calculated by time-dependent perturbation method using the CNDO/S method.

When the calculated β values are plotted against the number (**n**) of component moieties (Fig. 5), it is evident that the additivity of β is one of the main reasons for the high SHG of these systems (main-chain type liquid crystalline polymers).

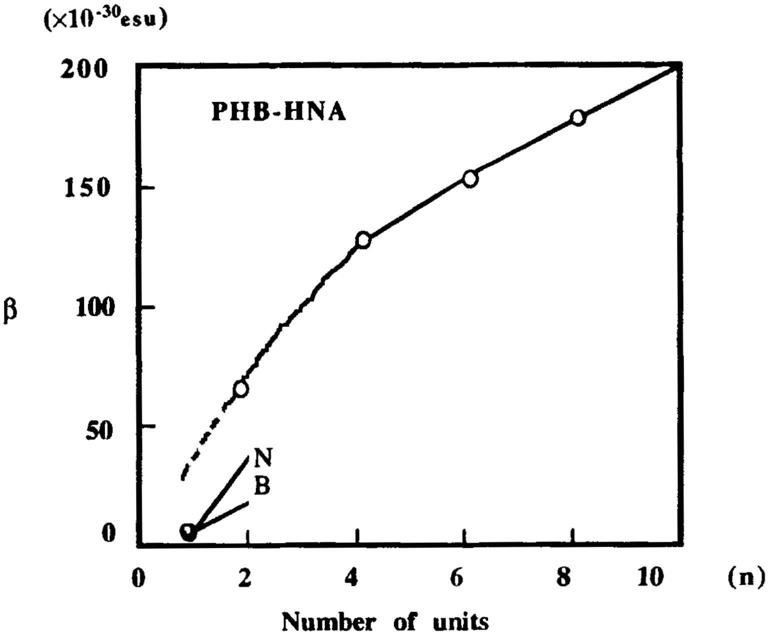


FIGURE 5 Calculated hyperpolarizability (β) against the number of units.
B: a single PHB, N: a single HNA

Second Harmonic Generations and Structure of the Mechanically Oriented Samples

It was found that the SHG of the film was greatly affected by the processing conditions. In our experiment, a new alignment technique was developed to get a high SHG of the film. The Liquid Crystalline Polymer (LCP) was firstly molten into liquid crystalline state, and then instantly stretched by two sets of rollers along two-opposite-way. The SH intensities of some films are shown in Fig. 6 . As obviously seen from the Figures, SH intensities are observed when the directions of electric vector of incident light are coincide with the direction of molecular long axis. The NLO coefficients of the films formed in various conditions are shown in Table II, compared with the value of a standard Y-cut quartz. It can be seen that the SHG intensity of the film formed by this new technique (Sample A) is improved by above twice as large as the films formed in a usual T-die extrusion (Sample C) and a bit higher than that of a roller extension (Sample B). Up to now, the largest second nonlinear coefficient d_{33} of the film is above 10 × d_{11} (quartz) measured by Marker Fringe method[11]. It is suggested that the crystal orientation of the film formed in this new way is the highest, compared with the others, the solid structures of which have been characterized by polarized microscope and X-ray diffraction. Fig. 9 is an X-ray diffraction pattern of the films formed in different

conditions, respectively. Many investigations on the crystalline structure of these copolymers by X-ray method have been reported especially by Blackwell et al[14]. However, hardly any definite structure is approved among researchers.

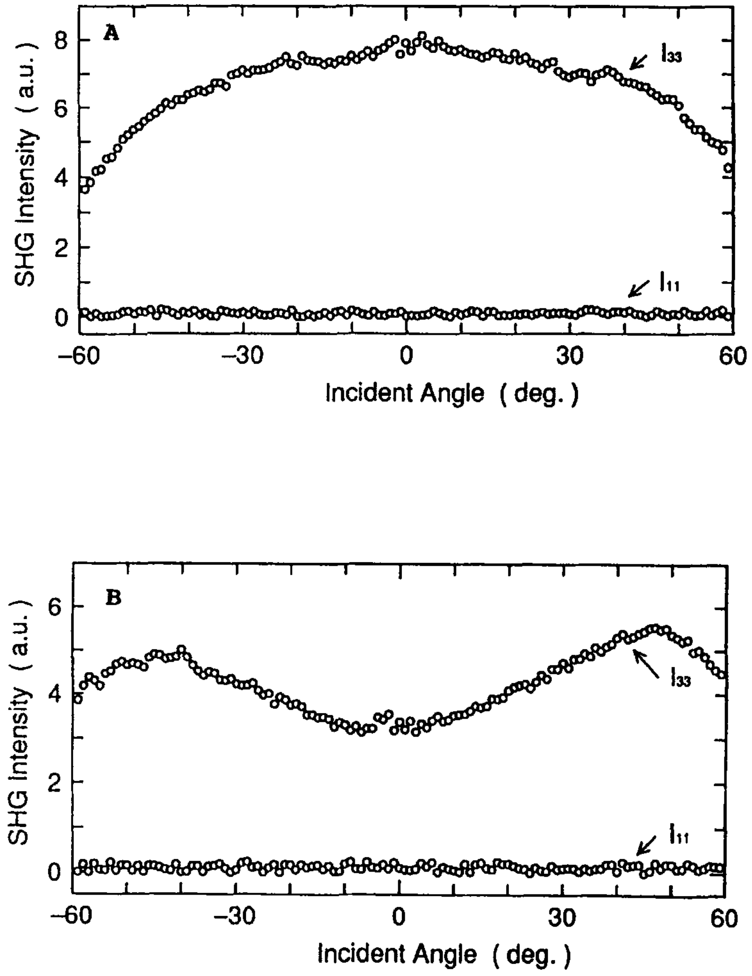


FIGURE 6 SHG intensities of PHB / HNA film against incident angle.

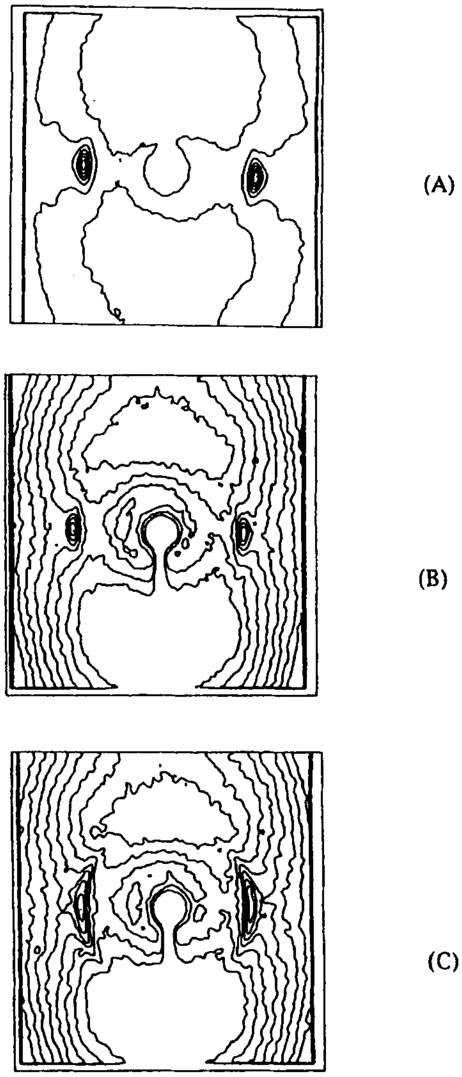


FIGURE 7 X - ray diffraction patterns of the films obtained in three different ways (A, B, C).

TABLE II Nonlinear optical coefficients of the PHB/HNA mechanically oriented films

Sample	Thickness(μm)	d_{exp}[x d_{11}(Quartz)]	d_{exp} (esu)
A	16	11.5	1.4×10^{-8}
B	18	10.5	1.3×10^{-8}
C	20	6.2	7.4×10^{-9}

conditions, respectively. Many investigations on the crystalline structure of these copolymers by X-ray method have been reported especially by Blackwell et al[14]. However, hardly any definite structure is approved among researchers.

Second Harmonic Generations of the Poled Samples

SHG for the samples using sandwich cell

The film sample made by the double orientation method (roller extension method) with the PHB:HNA composition of (60:40) gave an effective NLO coefficient $d_{exp} \cong 10$ times as large as that of the quartz d_{11} value, that is, 5pm/V, reported previously[10]. In such film samples, the molecules are highly oriented being parallel to the machine direction. However, the polarization direction of the molecules may not be entirely the same. Since we expect to obtain a more effective SHG sample when the polarization direction is the same for all molecules in the film, we performed several trials of DC electric field application, and determined the conditions to obtain an electric field oriented (i.e., poled) large monodomain sample. As reported previously[13], the molecular orientation reaches a steady state corresponding to the voltage within 2-5 min. and the sample attains an electrically oriented monodomain-like state, ascertained by the polarized microscopic observation.

The conditions determined by the above method were applied DC voltage of 8-12kV/cm at 290°C. The best temperature was at a constant temperature between 285 to 290°C.

SHG for the sample using transverse cell

Taking the above result into account, the electrically oriented (E-2) samples with a thickness and a width of 30μ and 1mm, respectively, were prepared, using the electric field horizontally (transversely) applied cell (Fig. 2). Thus the SHG efficiency and the effective NLO coefficient d_{exp} were evaluated for the electrically oriented (E-2) film samples. The d_{exp} of each sample was evaluated by the Maker Fringe Method and also by the measurements of conversion efficiencies and Yariv's Equation[12]. The d_{exp} values thus determined for the electrically oriented (E-1) and (E-2) samples two or three times as large as that of the mechanically oriented sample. d_{exp} (electrically oriented) $\cong$ 10 - 15pm/V.

SHG for the samples prepared by corona-poling

SHG of the corona-poling samples are rather weak than expected. One of the reason for this, the molecular orientation is not sufficient, which is observed in the Maker Fringe measurement and also even by polarizing microscope. At present we attain almost half as large as that of the above two electrical applied samples.

Trials of Quasi-Phase Matching by Using Mechanically Oriented Samples

Quasi-phase matching by using mechanically oriented samples

It has been known that the alignment of periodically inverted-polarized domains can make quasi-phase matching and often shows high SH efficiency. Here, the quasi-phase matchings were tested using mechanically oriented samples because those films were obtained largely at one time and that have rather smoother surfaces.

As shown in Fig. 8 schematically, a periodically inverted-polarized domain is easily obtained by piling the films so that the machine directions of the films change alternatively, keeping opposite directions with each other.

A system of 4 or 5 sheets improve the SH efficiency. When we add thin appropriate liquid crystal films between those oriented polymer films and on the surfaces, the SH efficiency increase more than 4~5 times than otherwise. The appropriate liquid crystal does mean that it has adequate refractive index matching with those polymer films.

The schematic picture of the device is shown in Fig. 9. In this Figure, the liquid crystal (Nematic)films are represented by thick solid line.

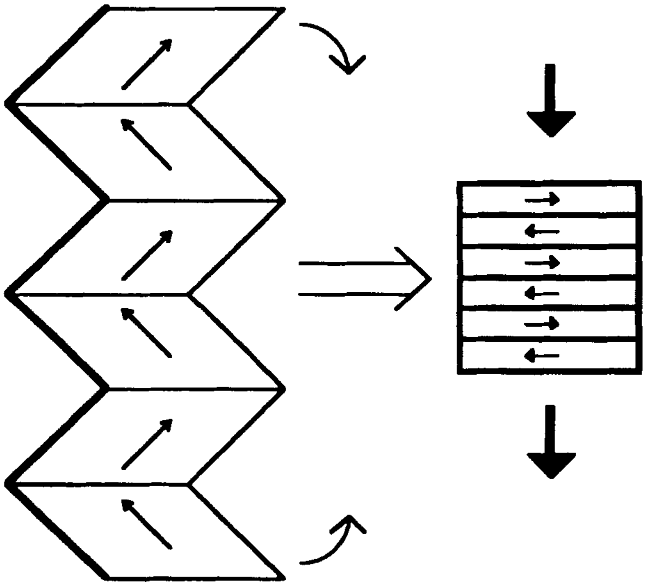


FIGURE 8 Schematic representations to make inverted - polarized piled films. The thin arrows show the machine direction.

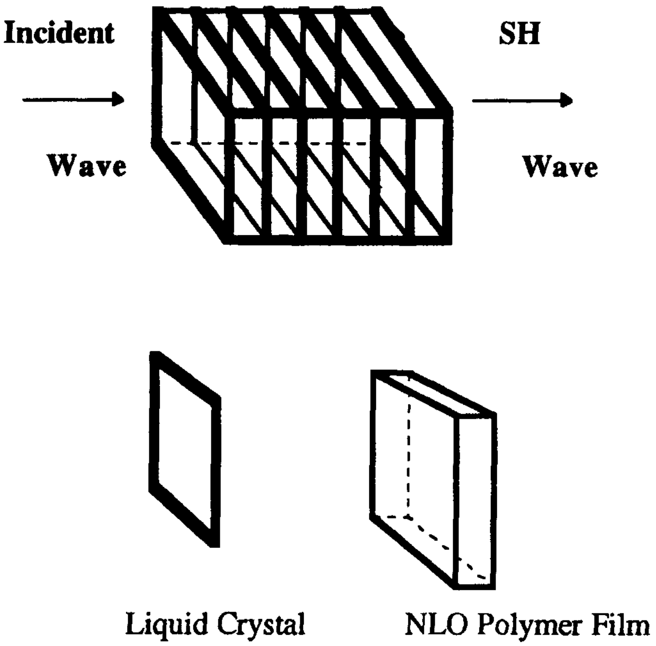


FIGURE 9 Schematic representation the piled structure of NLO polymer films and liquid crystal films.

Alternation SH efficiency by applying electric field

In Fig. 10, a schematic picture of the device which can change SH efficiency by applying electric field is shown. When we apply voltage between electrode, the SH efficiency increases and decreases depending on applied voltage, thus one can control the SH efficiency by applying voltage[high frequency (5Khz), AC]. Around 1 volt/10(µ) gives increasing SH efficiency twice as much as that of non-voltage application.

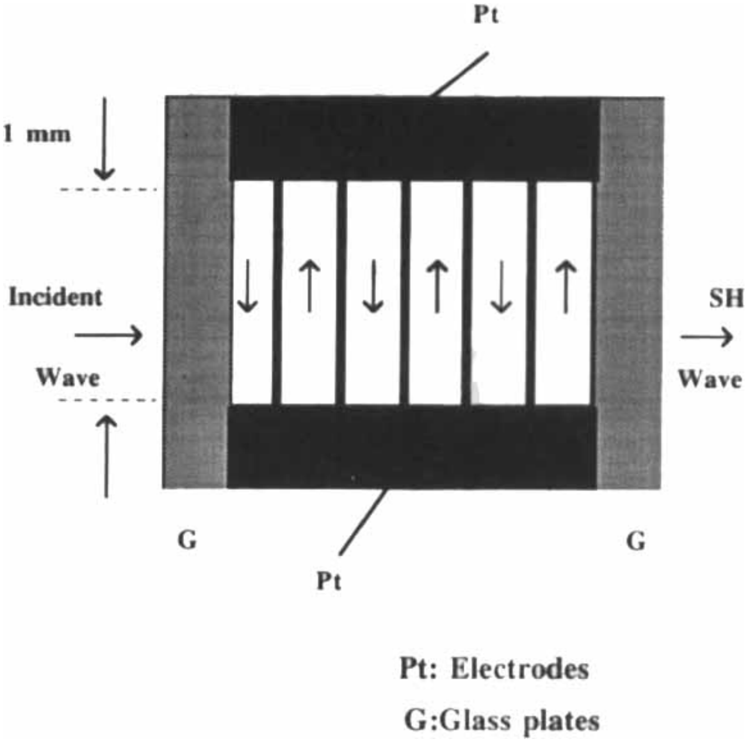


FIGURE 10 Schematic picture of the device which can control SH efficiency by electric field application inverted - polarized piled films.

Acknowledgments

The author is grateful to Dr. Lonnie Bryant and Dr. Nakazono of KRI International, Inc. (Kyoto). Dr. Bryant supplied us with various samples, and Dr. Nakazono helped us to determine the Degree of Polymerization of sample polymers by ^{1}HNMR method. We are also grateful to Dr. Saijyo and Mr. Jiang of our department who helped us doing the X-ray measurements. This work was supported partly by a Grant-in-Aid for Scientific Research on

Priority Areas of the Ministry of Education, Science, Sports and Culture, Japan (No. 09222213).

References

[1.] J. D. Mackenzie, C. Y. Li, Xu, and Yuhuan, *Chem. Express*, **6(12)**, p.903, 1991.

[2.] K. D. Singer, M. G. Kuzyk, and J. E. Sohn, *Opt. Soc. Am.* **B 4**, p.968, 1987.

[3.] H. Nakanishi, *Solid Physics*, **24(11)**, p.873, 1989.

[4.] A. Kamal, D. Weinberger, and W. Weber, *Opt. Lett.* **15**, p.613, 1990.

[5.] L. M. Hayden, G. F. Santer, F. R. Ore, and P. F. Pasillas, *J. Appl. Phys.* **68(2)**, p.456, 1990.

[6.] E. Kuchiki, A. Kidoguchi, T. Watanabe, and S. Miyata, *Kobunshi Ronbunshu*, **47(11)**, p.863, 1990.

[7.] H. Matsuda, *Kobunshi*, **40(5)**, p.324, 1991.

[8.] S. Umegaki, *Sen-i Gakkai Preprints*, **G123**, 1994.

[9.] G. R. Meredith, J. G. Vanadusen and D. J. Williams, *Nonlinear Optical Properties of Organic and Polymeric Materials, ACS Symposium Series*, p.109, 1983.

[10.] H. Tanaka, and T. Asada, *Polymer Preprints, Japan*, **40(10)**, p.3645, 1991. T. Asada, *Mol. Cryst. Liq. Cryst.* **254**, p.125, 1994.

[11.] J. Jerphaganon, and S. K. Kurtz, *J. Appl. Phys.* **41**, p.1667, 1970.

[12.] A. Yariv, *Quantum Electronics*, p.393, John Willy & Sons, New York, 1989.

[13.] T. Asada and H. Tanaka, *Mol. Cryst. Liq. Cryst*, **299**, p.85, 1997.

[14.] R. A. Chivers, J. Blackwell, and G. A. Gutierrez, *Polymer*, **25**, p.435, 1984.

[15.] J. P. Stewart, *J. Comput. Chem.* **10**, p.209, 1989.