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

Optical Second-Harmonic Generations of Liquid Crystalline Main-Chain Polymers

Tadahiro Asada [a]

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

Version of record first published: 24 Sep 2006.

To cite this article: Tadahiro Asada (1994): Optical Second-Harmonic Generations of Liquid Crystalline Main-Chain Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 254:1, 125-135

To link to this article: http://dx.doi.org/10.1080/10587259408036074

Mol. Cryst. Liq. Cryst. 1994, Vol. 254, pp. 125–135
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

OPTICAL SECOND-HARMONIC GENERATIONS OF LIQUID CRYSTALLINE MAIN-CHAIN POLYMERS

TADAHIRO ASADA
Department of Polymer Chemistry,
Kyoto University, Kyoto 606, Japan.

(Received: February 7, 1994)

Abstract Optical second-harmonic generation (SHG) of liquid crystalline main-chain polymers, which are the copolymers of 2-hydroxy-6-naphthoic acid with 4-hydroxybenzoic acid, and their application for SHG device have been studied. Varieties of copolyesters which have various composition-ratios were prepared. The SHG activities of each sample were evaluated by both the powder and Marker fringe methods. It was found that the double orientation processing was effective to obtain the sample of high SHG activity. At present, the effective nonlinear optical coefficient d(eff) of the sample with the composition PHB/HNA (60/40), which was prepared to be a plane-plane oriented (double orientation) film of thickness 10-30μm, is obtained to be 10 times that of quartz d_{11} value (0.50pm/V).

INTRODUCTION

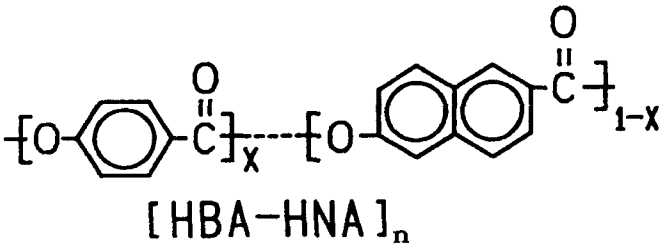
Nonlinear optical properties of low molecular-weight organic materials have been extensively studied in this decade. However, these materials are known to have less stability. To improve the stabilities and processabilities, blend or graft-polymerization of nonlinear optical organic substances with polymers has been intensively studied by many researchers[1-3]. There, however, still remain stability problems. To the contrary, we have pointed out some liquid crystalline main-chain polymers show large second harmonic generation (SHG)[4]. They are expected to be stable and good nonlinear optical materials for various

applications, because these materials have been developed to be high performance materials. Moreover, in the case of main-chain type, polymeric effect, i.e. the accumulating effect of the optical properties of individual units can be expected, if the polymerization is performed adequately. In this work, optical second-harmonic generation (SHG) of liquid crystalline main-chain polymers and the possibility of their application for SHG devices have been studied.

EXPERIMENTAL

MATERIALS

The thermotropic liquid crystalline main-chain polymers studied were mainly copolyesters of HBA and HNA:



Varieties of copolyesters which have various composition ratios were prepared: the molar ratio of HBA:HNA = (90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90) etc.

REPARATION OF FILM SAMPLES

To obtain a more or less doubly oriented film sample, roller extension method right after fiber extrusion were used to prepare a film sample. The schematic diagram is

shown in Fig.1.

APPARATUS AND MEASUREMENTS

The apparatus used for SHG studies mainly an optical system for Maker fringe measurement according to J. Jerphagnon and S. K. Kurts[5]. Nd:YAG lazer (Spectron Co. Ltd., SL401) was used as a light source for the fundamental light wave (wavelength=1064nm). The generated second harmonic wave in a sample was picked up by using a monochromater (Jasco, CT-10) to be detected by a photomultiplier tube (Hamamatsu photonics Co. Ltd., R1387). A rotating stage (Aerotech Inc. Co., ART50M) was used for a sample to measure the intensity of generated second harmonic wave as a function of incident angle. To warrant our apparatus for SHG measurement, Maker fringe measurements for three different standard Y-cut quartz with different thickness were performed.

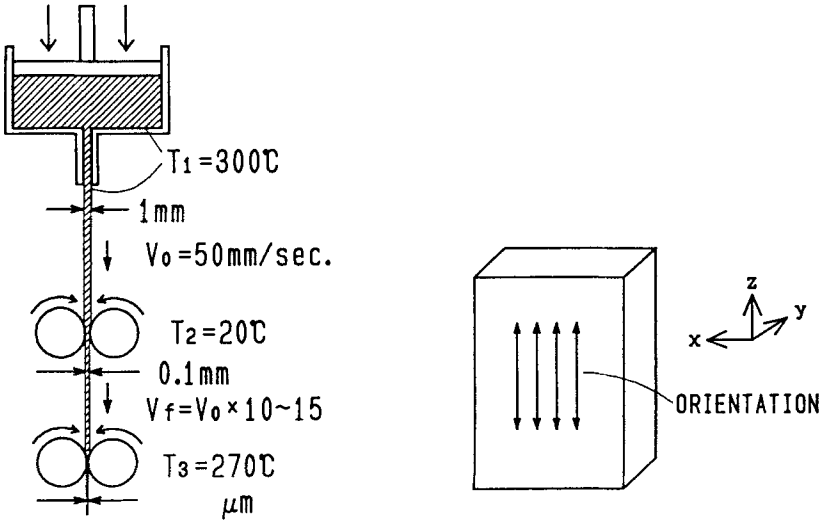


FIGURE 1 Schmatic diagram of roller extension method and the reference axes of the film.

By applying curve fitting method to the observed results, the d_{11} values were evaluated for each Y-cut quartz plate, and compared with each other. This experiment warranted that our apparatus gave precise data. In Figure 2, the geometries for the Maker fringe measurements in our studies are shown. In these case (both the electric vector of fundamental wave and that of generated second harmonic wave are parallel to the rotation axis of a sample), the intensity $I_{2\omega}$ of the generated second harmonic wave will be represented by Eq.(1), provided there is no light scattering and no

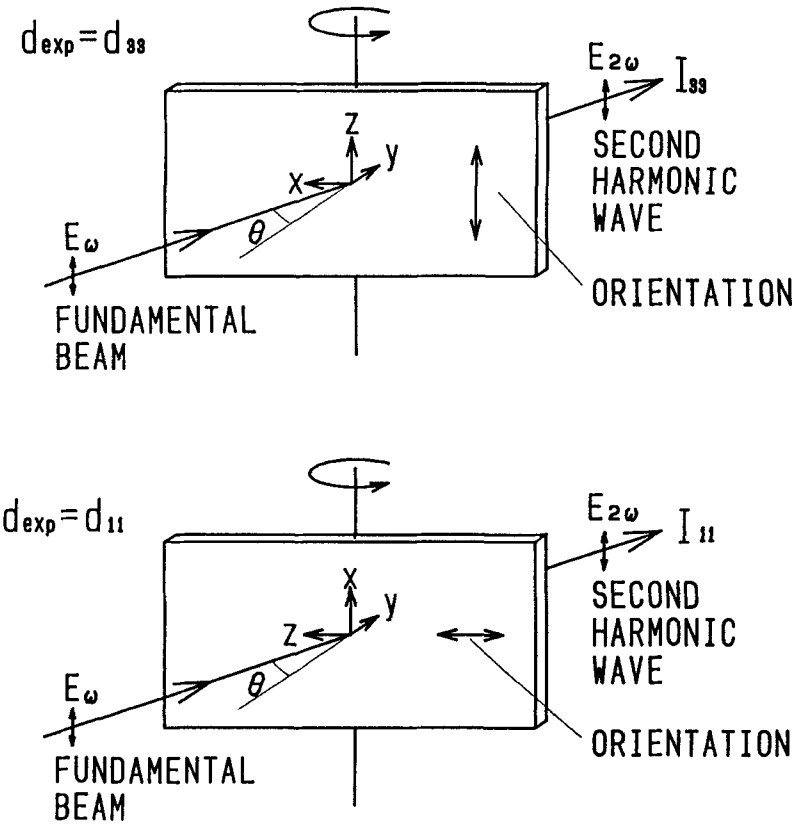


FIGURE 2 Optical geometries for the measurements.

absorption. Eq.(1) gives the relation between $I_{2\omega}$ and Non-linear optical coefficient d.

$$I_{2\omega} = (512\pi^3 / A) t_\omega^4 T_{2\omega} I_\omega d^2 [1 / (n_\omega^2 - n_{2\omega}^2)]^2 \sin^2 \Psi \quad (1)$$

$$t_\omega = \frac{2 \cos \theta}{n_\omega \cos \theta + \cos \theta_\omega'}$$

$$T_{2\omega} = \frac{2 n_{2\omega} \cos \theta_{2\omega}' (n_\omega \cos \theta + \cos \theta_\omega') (n_{2\omega} \cos \theta_\omega' + n_\omega \cos \theta_{2\omega}')}{(\cos \theta + n_{2\omega} \cos \theta_{2\omega}')^3}$$

$$\Psi = \frac{2\pi L}{\lambda} (n_\omega \cos \theta_\omega' - n_{2\omega} \cos \theta_{2\omega}')$$

$$\theta_i' = \sin^{-1} \left(\frac{\sin \theta}{n_i} \right)$$

,where I_ω, A, n_ω, and $n_{2\omega}$ are, respectively, the intensity of the incident fundamental wave, the area of the cross section of the beam, the refractive index of the sample for the fundamental wave, and the refractive index of the sample for the generated second harmonic wave. L and θ are, respectively, the thickness of the sample and incident angle of the beam. t_ω and $T_{2\omega}$ are, respectively, the transmission factors of the sample for the light of frequency ω and 2ω.

Eq.(1) will be rewritten simply by Eq.(2), where C is a constant and independent of a sample and θ, provided the measurements will be done under the same conditions. In Fig.3, calculated Maker fringe curve and its conponent curves $[cd^2F(\theta)]$ and $G(\theta)$ for a Y-cut quartz of thickness 1.5mm, as an example. As seen from the Figure, the front term of the equation(2) show arch figure which has maximum at $\theta=0$, and $G(\theta)$ term vibrate between 0 and 1. The resulted curve, i.e. the product of both terms show typical Maker fringe curve. In case, the sample thickness is greatly larger than coherent length,

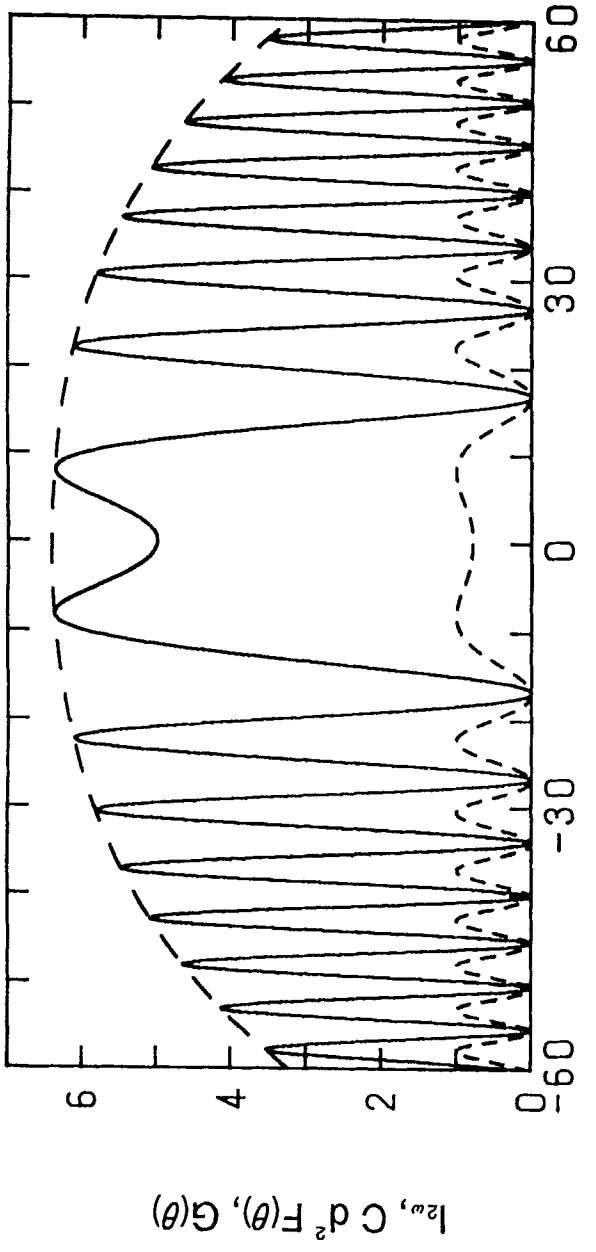


FIGURE 3 Calculated Marker fringe curve by Eq.(2).

typical Maker fringe curve can be expected. For such case, we can evaluate d from $cd^2F(0)$, while in case the thickness not large enough such fringe curve can not be obtained. Such a case we must obtain d value by curve fitting method using full of Eq.(2) and cd^2 value of a standard sample (for example, Y-cut quartz).

$$I_{2\omega} = C\, d^2\, F(\theta)\, G(\theta) \qquad (2)$$

$$F(\theta) = [\, 1 / (\, n_{\omega}^2 - n_{2\omega}^2 \,)]^2\, t_{\omega}^4\, T_{2\omega}$$

$$G(\theta) = \sin^2 \Psi$$

$$C = (\, 512\, \pi^3 / A \,)\, I_{\omega}$$

To measure the refractive index, a modified Abe type refractmeter (1T, ATAGO Co. TOKYO) with CCD detector and CRT monitor was used.

RESULTS AND DISCUSSION

Sample films were prepared by previously described double orientation method. First of all, the nonlinear optical properties of two film samples of HBA-HNA (60/40) prepared with different roller extension conditions will be introduced. The dispersions of the obtained refractive index of HBA-HNA film (A) are shown in FIg.4. From the experimental curves, n_z and n_x at fundamental wavelength (1064nm) and second harmonic wavelength (532nm) were evaluated by extrapolation and interpolation. These experimental results coincide well with the Sellmeir's dispersion formula. The coherent length l_c of the material will be obtained by Eq.(3).

$$l_c = \lambda / 2(n_{2\omega} - n_{\omega}) \qquad (3)$$

Maker fringe measurements were done two different optical geometries shown in Fig.2. The films of

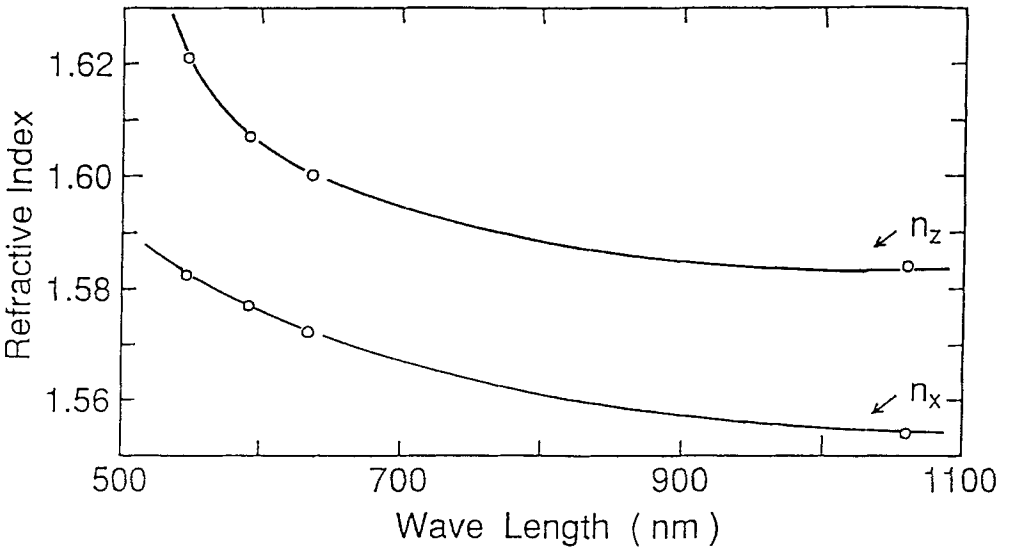


FIGURE 4 Dispersion of the refractive index of HBA/HNA film (A).

main-chain type LC polymer are not necessarily complete crystal, but the intensity of second harmonic wave observed at the Geometry(a) in Fig.2 will represent as I_{33} and obtained nonlinear optical coefficient as d_{33}, according to the reference axes shown by Fig.2, for convenience. The values obtained from the Geometry(b) in Fig.2 represent as I_{11} and d_{11}. The obtained results of SHG for sample A and B are shown in Fig.5(a) and Fig.5(b). From the figures, the intensity of the generated second harmonic wave is observed appreciably, only when the orientation direction of the molecule and the electric vector coincide with each other. SHG concerned with I_{33} will be discussed, hereafter.

The curve fitting results are shown in Fig.6(a) and (b) for both sample A and B. The evaluated d values summarized in Table 1 with other characteristic values of the films.

One can expect the HBA-HNA films to be stable

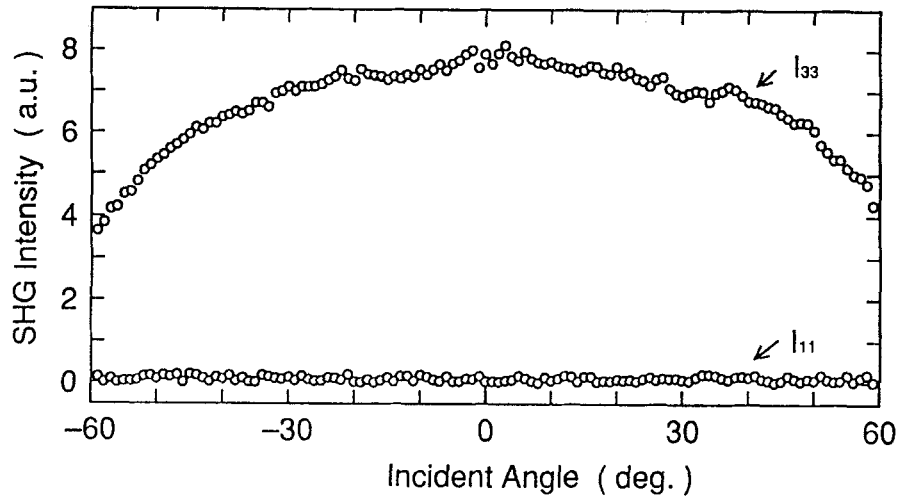


FIGURE 5(a) SHG intensity of Sample A.

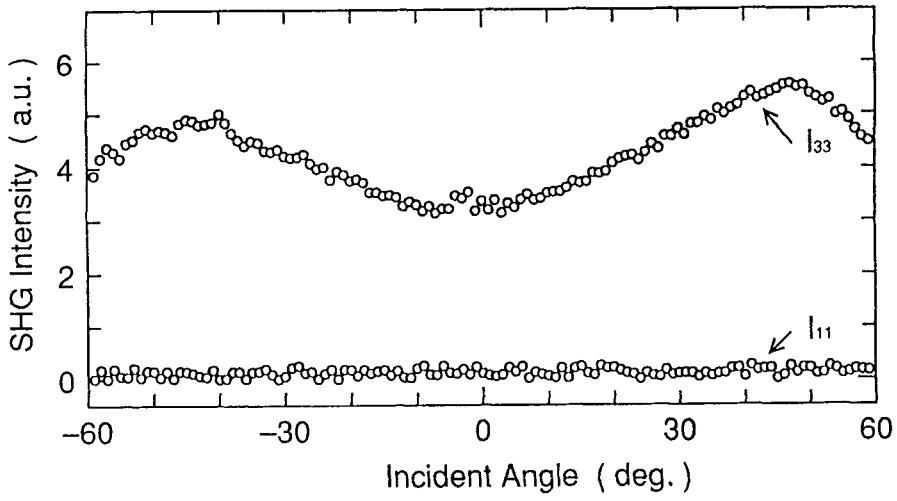


FIGURE 5(b) SHG intensity of Sample B.

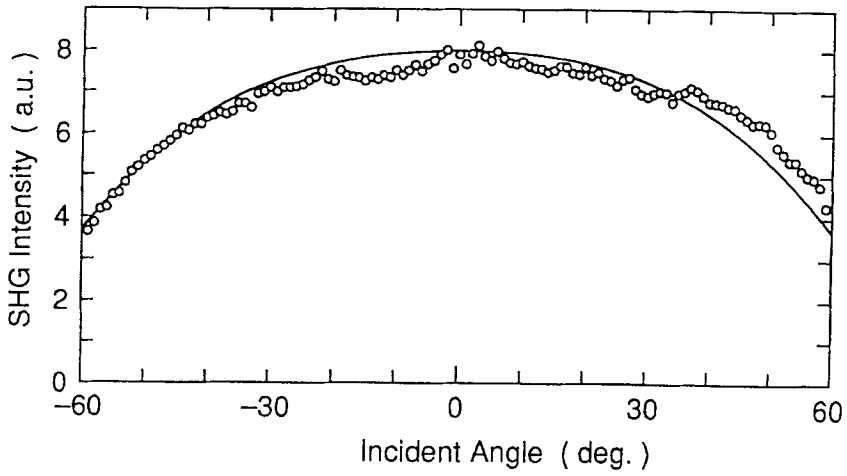


FIGURE 6(a) SHG intensity of Sample A.
o:Experimental data
-:Calculation curve by Eq.(2)

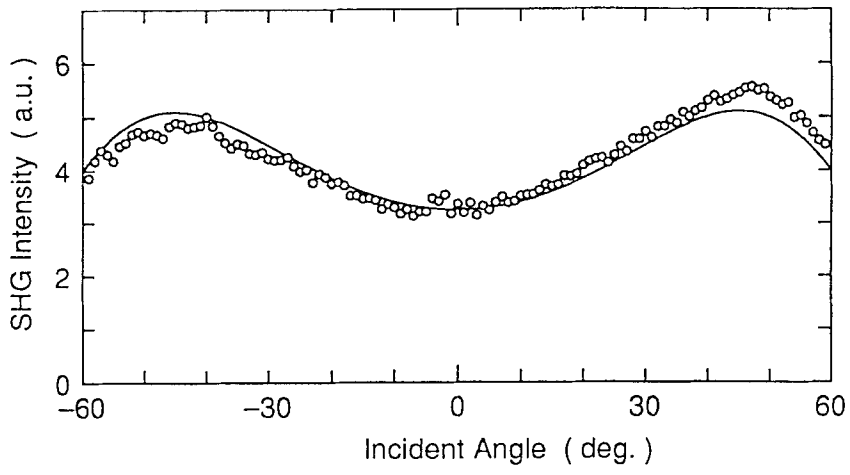


FIGURE 6(b) SHG intensity of Sample B.
o:Experimental data
-:Calculation curve by Eq.(2)

TABLE 1

Nonlinear optical coefficients of the PHB/HNA films

Sample	Thickness (μm)	d_{exp}[x d_{11}(Quartz)]	d_{exp}(esu)	α
A	18	10.7	1.3×10^{-8}	16°
B	22	9.3	1.1×10^{-8}	23°

α: a measure of an orientation degree (the angle of arc of X-ray diagram at $2\theta \neq 19^{o}$)

nonlinear optical materials. The films are expected to be used as a filter which can change the wavelength of a given light.

ACKNOWLEDGMENT

The author thanks to Drs. H. Yokomichi and T. Fujiwara (Advanced Research Institute of Osaka Gas Co., Osaka, Japan) for helpful discussion.

REFERENCES

1. J. D. Makenzie, C. Y. Li, and Y. Xu, Chem. Express, 6, 903 (1991).
2. K. D. Singer, M. G. Kuzyk, and J. E. Shon, J. Opt. Soc. Am., B4, 968 (1987).
3. H. Nakanishi, Solid Physics, 24, 873 (1989).
4. H. Tanaka and T. Asada, Polymer Preprints, Japan, 41(3), 785 (1992).
5. J. Jerphagonon amd S. K. Kurts, J. Appl. Phys., 41, 1667 (1987).