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T. Asada [a] & H. Tanaka [a]

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

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NONLINEAR OPTICAL PROPERTIES OF THE THERMOTROPIC LIQUID-CRYSTALLINE MAIN-CHAIN POLYMERS (AROMATIC POLYESTERS)

TADAHIRO ASADA* and HIROYUKI TANAKA
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, KYOTO, 606 JAPAN

Abstract The second harmonic generation (SHG) of the liquid crystalline main-chain type copolymers of 2-hydroxy-6-naphthoic acid (HNA) with 4-hydroxy-benzoic acid (PHB), in various composition ratios were investigated. The SHG of the films was greatly affected not only by the polymerization conditions but also by the processing conditions of the films. The nonlinear optical coefficient d_{exp} of the electrically oriented sample is 3-5 times larger than that of the mechanically oriented sample (5pm/V). The relationship between molecular compositions and the hyperpolarizability (β) examined by the molecular orbital method clearly indicated that the high SHG of the main-chain polymer mainly originates from the additivity of β value of individual unit due to head to tail connection.

INTRODUCTION

Blend or graft polymerization of nonlinear optical organic materials with polymers has been intensively studied by many researchers[1-3] to improve stability and processability. However, problems in the durability remained.[4] To the contrary, the main-chain type nonlinear optical polymers are expected to be durable and good for various applications, because these materials have been developed for high performance.

Some liquid crystalline polymers have been reported to exhibit very large optical nonlinearities.[5] The merits of the liquid crystalline polymers for the second harmonic generation (SHG) are that the molecular structure of a polymer chain is noncentrosymmetric and also they form highly oriented condensed state, when they are processed in the liquid crystal state.

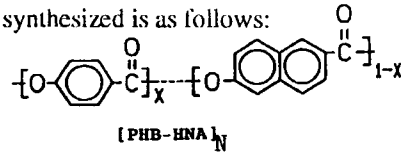
The SHG of the liquid crystalline main-chain type copolymers of 2-hydroxy-6-naphthoic acid (HNA) with 4-hydroxy-benzoic acid (PHB), in various composition ratios were investigated. The effect of DC electric fields application as well as the mechanical extension on the SHG efficiency was examined. The relationship between molecular compositions and the hyperpolarizability (β) was examined by the molecular orbital methods.

*corresponding author

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}H NMR 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 preparation procedure for electrically oriented samples will be described later.

Measurements

1) Nonlinear Optical (NLO) Properties

The SHG of the samples was evaluated by both the powder method (for as polymerized samples) and Maker Fringe Method.[6] The Nd: YAG laser (Spectron, SL401) was used as the light source (wavelength=1064nm). The experimental apparatus for SHG measurement has been described previously.[6] The second harmonic NLO coefficient d_{33} of the films was evaluated by the Marker Fringe Method[7], compared with standard Y-cut quartz d_{11}. In case it was difficult to use Maker Fringe Method to obtain d_{33} or d_{exp} and the conversion efficiency was possible to obtain, the effective NLO coefficient d_{exp} for a film sample was evaluated by using Yariv's Equation.[8]

2) 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 studies on the electric field applications, using DC electric fields will be reported here. A block diagram of the instrument for studying electro-optical properties is shown in Figure 1. It is constructed of three parts; optical system, hot stage(HS), and a cell for the liquid crystal sample(C). The video

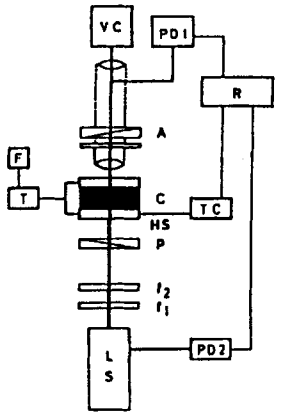


FIGURE 1 A block diagram of the instrument for the electro-optical properties.

HS: hot stage
C: cell for the liquid crystal sample
LS: white light source
P: polarizer
A: analyzer
PD1: photo detectors
VC: video camera
TC: thermo-controller

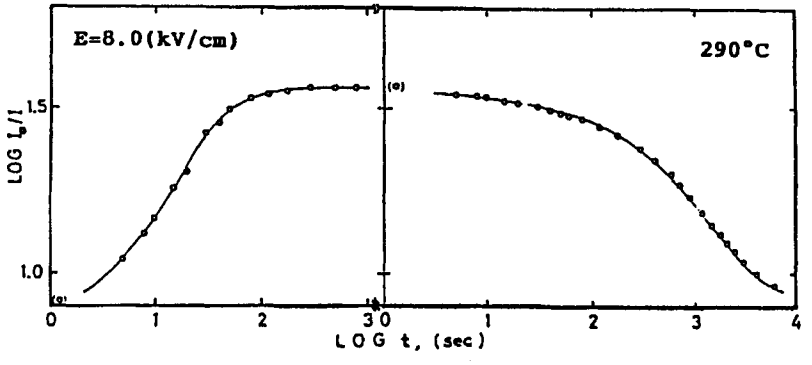


FIGURE 2 Change in light-transmittance when an electric field is applied and released (crossed polars).

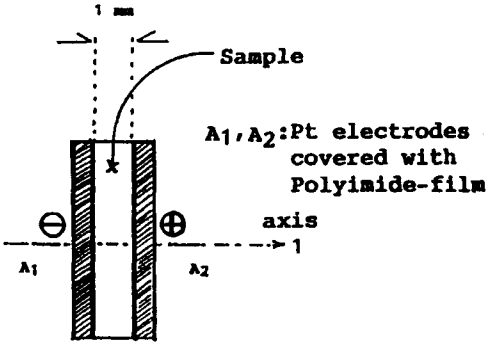


FIGURE 3 Transversely-applied electric field cell.

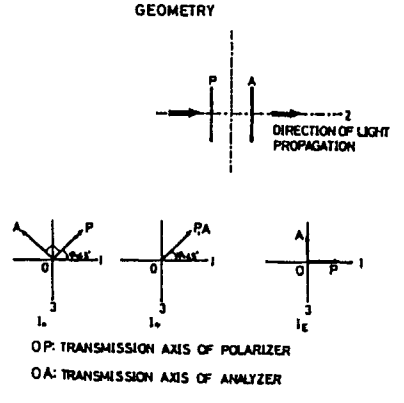


FIGURE 4 Optical geometry.

camera (VC) enables us to record the change of the image with time after onset or cessation of electric fields, as well as the observation by a microscope or measurements of transmitted light intensity (in this case, light source LS is replaced by He-Ne gas laser). For DC electric field application, a DC electric field power supplier was also used instead of the function generator (F) and transformer (T). The cell used had two parallel glass plates coated inside with conductive thin layers (In_2O_3) separated 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 and coincides 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. An example is shown in Figure 2. The $\log I_0/I$ is plotted against time, where I_0 and I represent the transmitted light intensities of parallel-polarizers geometry in blank and of crossed-polarizers with a sample, respectively. In this case (Case E-1), the orientation direction of the molecules is perpendicular to the film surface. To obtain a large monodomain sample easily, two sheets of newly cleaved mica film were used between the electrode and liquid crystalline sample to cover the surface of a liquid crystalline sample by the plane of cleavage. The birefringence effects arising from the mica film are canceled by using a compensator, beforehand. For comparison, electric field horizontally (transversely) applied cells (transverse cells) were also used (as shown in Figure 3, Case E-2). In this case, I_{χ} and $I_{//}$ were measured right after application or cessation of voltage. Optical Geometry is shown in Figure 4. From the changes of I_{χ} and $I_{//}$, the changes of optical retardation (birefringence × thickness) can be obtained by Equation (1) during the application or after cessation of voltage.[9,10] 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, an excess amount of liquid nitrogen was poured into the whole cell system instantly at the same time the heaters were switched off.

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

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.

RESULTS AND DISCUSSION

Effect of Electric Field Application for SHG

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} 10 times as large as that of the quartz d_{11} value, that is, 5pm/V, reported previously.[6] 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 expected 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 shown in Figure 2, 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 the constant temperature between 285 and 290°C. Taking into account the above results, the electrically oriented (E-2) samples with a thickness and width of 30μ and 1mm, respectively, were prepared (Figure 3.), using the electric field horizontally (transversely) applied cell. 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.[8] The d_{exp} values thus determined for the electrically oriented (E-1) and (E-2) samples were almost 3-5 times as large as that of the mechanically oriented sample. d_{exp} (electrically oriented)≅15-25pm/V.

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 hyperpolalizability (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. Here some examples of calculation by the molecular simulation method for this kind of polymer are given.

The calculation procedure is as follows : (1) A molecule is constructed by the component moieties. (2) optimized by using MNDO Parametric Method 3 (proposed by James J. P. Stewart[11]). (3) β is calculated by time-dependent perturbation method using the CNDO/S method.

As an example, the calculated β values are plotted against the number (n) of component moieties in Figure 5. From the Figure, 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).

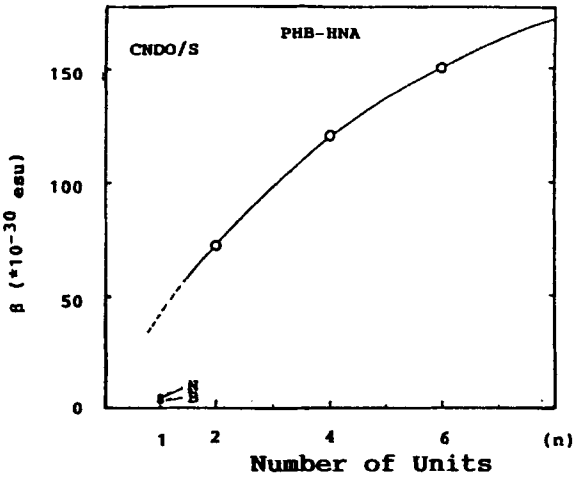


FIGURE 5 Calculated hyperpolarizability (β) against the number of units.
B: a single PHB, N: a single HNA

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