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### Orientational Properties in Nonlinear Optical Polymers of Azo-Containing Poly(dipropargyloxybenzoates)

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## **Orientational Properties in Nonlinear Optical Polymers of Azo-Containing Poly(dipropargyloxybenzoates)**

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*We discuss the second harmonic generation (SHG) properties for the newly synthesized ortho- and meta-polymers containing dipropargyloxybenzoates in the main chain and Disperse Red 1 in the side chain with an in-situ SHG measurement. The second harmonic signals for the ortho-polymer gradually increased with time for more than 2 hours and reached to a high signal level, while the ones for the meta-polymer quickly saturated at a low signal level. This result indicates that the ortho-polymer was aligned more easily than the meta-polymer, which leads to the larger order parameter and the larger SHG coefficients for the ortho-polymer.*

**Keywords:** diacetylene-containing azo polymer; *in-situ* SHG measurement; second-order nonlinear optical polymer; structural isomerism

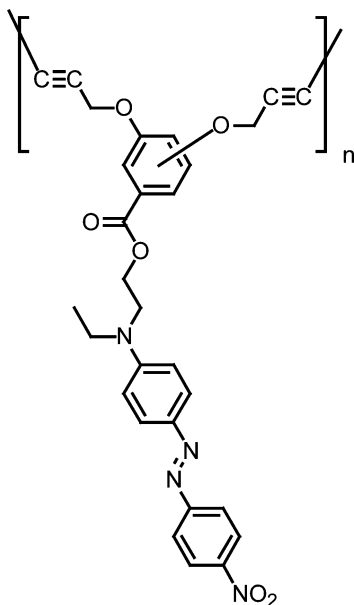
### **INTRODUCTION**

A great number of works on polymeric systems for second-order nonlinear optical (NLO) applications has been reported in the past decades [1–3]. However, their NLO responses, thermal stability, and mechanical properties are still insufficient for practical device applications. Normally, the development of NLO chromophore having large hyperpolarizability and an increase in the concentration of the NLO chromophore moiety have been tried to obtain high NLO responses.

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On the other hand, our main approach is the modification of the main-chain structure of the NLO polymers by changing the structural isomerism as well as increasing the chromophore concentration. Recently, we have reported that the novel diacetylene-containing NLO polymers which consist of rather rigid main chains and polar chromophore side chains showed the stable and high second-order NLO responses [4,5]. It was a very interesting result that the second harmonic generation (SHG) coefficients for poly(*para*-cinnamates) were about 4 times larger than those for poly(*meta*-cinnamates). This result indicates that the main chain conformation is also very important for the SHG properties of the NLO polymers.

In this work, as a continuation of the previous studies, we discuss SHG properties for newly synthesized *ortho*(3,4)- and *meta*(3,5)-polymers containing dipropargyloxybenzoates in the main chain and Disperse Red 1 in the side chain [6] in terms of the influence of the main-chain structure. Their chemical structures are shown in Figure 1. They have very high chromophore concentration of over 60%, calculated from the ratio of molecular weight of chromophore



**FIGURE 1** The chemical structures of *ortho*(3, 4)- and *meta*(3, 5) -polymers containing dipropargyloxy- benzoates in the main chain and Disperse Red 1 in the side chain.

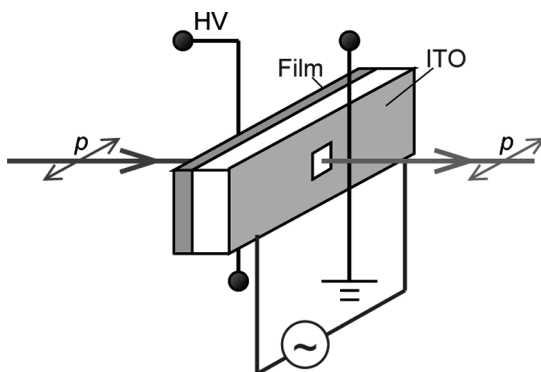
to that of the monomer unit. We will discuss the orientational dynamics for the both polymers by an *in-situ* SHG measurement.

## EXPERIMENT

The polymers were prepared by the method reported previously [6]. The glass transition temperatures for the *ortho*- and *meta*-polymers were determined to be 78 and 76°C, respectively, by thermal mechanical analysis (TMA) with a calorimeter (TMA 2940, TA Instruments). The polymers were soluble in N-methylpyrrolidone (NMP) and their inherent viscosities in NMP were found around 0.3 g/dl. The films were prepared by spin coating at 60°C on fused silica substrates for ellipsometry or ITO substrates for the *in-situ* SHG measurement. The films were dried in a vacuum oven at 80°C for 1 hour.

Spectroscopic ellipsometry was performed to determine the refractive index for the polymers. Ellipsometric data were acquired with a spectroscopic ellipsometer (M-150, JASCO), and the refractive indices were determined by modeling the polymers with two Lorentz oscillators using an analyzing software (MW-305, JASCO).

In order to observe electric-field induced alignment, an *in-situ* SHG measurement was performed at a fundamental wavelength of 1064 nm (a Q-switched Nd:YAG laser, DCR-130, Spectra-Physics). The transmitted second harmonic (SH) beam from the polymers was measured by a photomultiplier and a boxcar integrator. In order to heat the polymer films, the films were prepared on the glass side of ITO substrates with optical window, and AC voltage was applied to the ITO film (Fig. 2). Two tungsten wires were placed above the sample to perform corona discharging. Maker fringe method was also performed



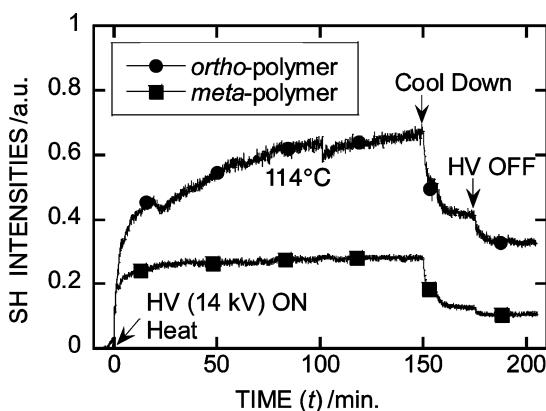
**FIGURE 2** Schematic representative of *in-situ* SHG measurement.

to determine SHG coefficients  $d_{33}$  and  $d_{31}$ . SH intensity for Y-cut quartz ( $d_{11} = 0.3 \text{ pm/V}$ ) was measured as reference data.

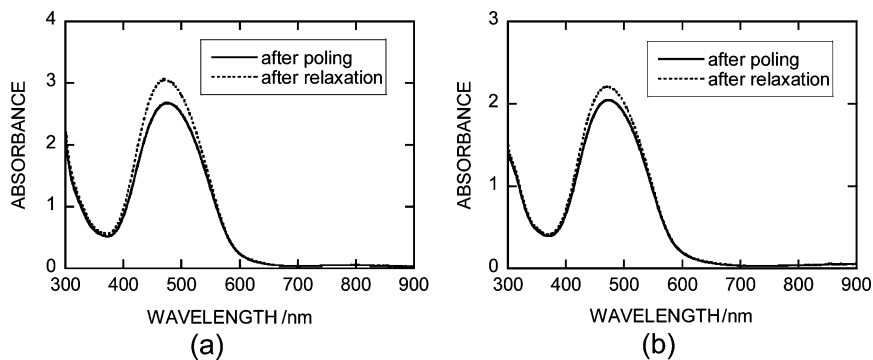
## RESULTS AND DISCUSSION

Figure 3 shows poling dynamics measured by the *in-situ* SHG measurement system. The SH signals for both polymers monotonously increased by heating the samples with a high electric field. However, the poling dynamics was different in these two polymers. The SH signals for the *ortho*-polymer gradually increased with time for more than 2 hours and reached to a high signal level, while the ones for the *meta*-polymer quickly saturated at a low signal level. This result might mean that, in the *meta*-polymer, it's difficult to obtain large order parameters with the orientation of the whole molecules although it's easy to align the NLO chromophore moiety in the free volume.

The alignment of chromophore moiety was also confirmed by the change of absorbance. Figure 4 shows the absorption spectra after poling and after relaxation. The orientational relaxation was confirmed by the SHG measurement. We obtained the larger order parameter for the *ortho*-polymer than that for the *meta*-polymer under the same poling condition. The order parameters were 0.13 and 0.07 for the *ortho*-polymer and the *meta*-polymer, respectively. This result also



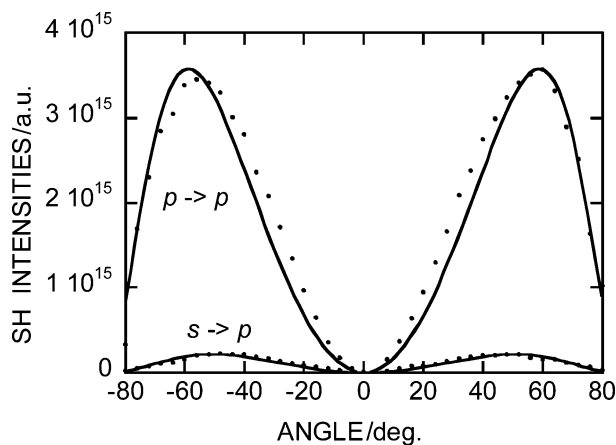
**FIGURE 3** Poling dynamics measured by the *in-situ* SHG measurement. High voltage (HV) of 14 kV was applied to the tungsten wires at  $t = -3$ , the sample was heated to a temperature of  $114^\circ\text{C}$  at  $t = 0$ , and cooled at  $t = 150$ , and HV was turned off at  $t = 175$ . The temperature of the sample reached to more than  $110^\circ\text{C}$  in 2 minutes after heating, and decreased to less than  $40^\circ\text{C}$  in 2 minutes after cooling.



**FIGURE 4** Absorption spectra after poling and after orientational relaxation by heating for (a) the *ortho*-polymer and (b) the *meta*-polymer.

shows that chromophore alignment in the *ortho*-polymer is easier than that in the *meta*-polymer.

Finally, we performed Maker fringe method to determine the SHG coefficients (Fig. 5). Table 1 shows the SHG coefficients and the order parameters for both polymers. The SHG coefficients  $d_{33}$  were 54.0 and 10.7 pm/V for the *ortho*-polymer and the *meta*-polymer, respectively. The *ortho*-polymer showed the larger SHG coefficients than that of the *meta*-polymer, as expected from the other experiments. These results indicated that the *ortho*-polymer was aligned more easily than



**FIGURE 5** Maker fringes for the *ortho*-polymer. The labels (s, p) represent the polarization of fundamental and second harmonic waves.

**TABLE 1** SHG Coefficients and Order Parameters for the *Ortho*- and *Meta*-Polymers

	$d_{33}$	$d_{31}$	$\Phi$
<i>ortho</i> -polymer	54 pm/V	18 pm/V	0.13
<i>meta</i> -polymer	11 pm/V	14 pm/V	0.07

the *meta*-polymer, which leads to the larger order parameter and the larger SHG coefficient for the *ortho*-polymer. The difference of the orientational properties between these two polymers is presumably due to the main-chain structure, because only the structural isomerism in the main chain is different.

## CONCLUSION

The orientational dynamics for *ortho*- and *meta*-polymers containing dipropargyloxybenzoates was discussed by the *in-situ* SHG measurement. This study shows that the structural isomerism of the main chain is important for the SHG properties in the poly(dipropargyloxybenzoates) as well as in the poly(cinnamates). It is possible to enhance the order parameter and the SHG coefficients by the optimization of the main chain conformation.

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