

SECOND-ORDER NONLINEAR OPTICAL SUSCEPTIBILITIES OF POLY[(HEXA-2,4-DIYNYLENE-1,6-DIOXY)DIBENZOATES] CONTAINING AZO CHROMOPHORE *DISPERSE RED 19* BY ELECTROABSORPTION SPECTROSCOPY

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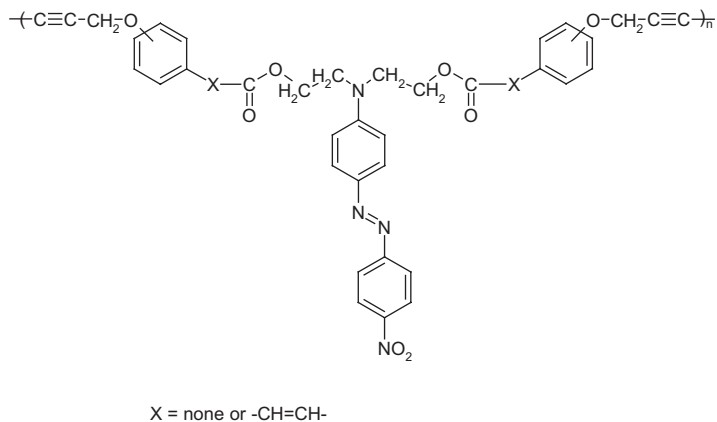
The second-order nonlinear optical susceptibilities $\chi^{(2)}$ of two isomeric polymers containing an azo dye, *Disperse Red 19*, were determined by the first-order electroabsorption spectroscopy (EAS), and compared with values previously obtained by SHG measurements. The *para*-polymer was found to have higher susceptibility than the corresponding *meta*-polymer. $\chi^{(2)}$ were found to be $5\text{--}6 \times 10^{-8}$ esu, which are comparable to those obtained by the Maker Fringe method.

Keywords: Electroabsorption spectroscopy; azo-polymers; second-order nonlinear optical susceptibility.

1. Introduction

Organic polymers that have second-order nonlinear optical (NLO) susceptibility were intensively explored by many researchers in the last decades. However, no materials were found to satisfy every requirement for device applications, and the research in this field slowly faded in recent years. The principal reasons for this are poor second-order NLO coefficients, and poor SHG stability due to inevitable relaxation of poled chromophores. Recently, we have reported some new types of polymers based on rigid main chain and azobenzene side chain (Scheme 1).

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Scheme 1. Poly(hexa-2,4-diynylene-1,6-dioxydibenzoates) and poly(hexa-2,4-diynylene-1,6-dioxydicinnamates) containing *Disperse Red 19*.

They presented very high SHG coefficients as high as 250–350 pm/V.^{1,2} This result demonstrated that the polymer main chain conformation is very important for SHG response of polymeric materials: the *para*-benzoate and *para*-cinnamate polymers had about three to five times greater SHG coefficients than the corresponding *meta*-polymers. Unlike the commonly investigated SHG polymers of the polymethacrylate type, these rather rigid main chain polymers seem to have less distortion in the main chain conformation when poled, and therefore, the orientation of chromophores can be maintained, resulting in extremely high SHG coefficients. Furthermore, these polymers can be cross-linked by UV irradiation at the poling temperatures through their diacetylene groups, so that the films are converted into totally hard thermoset polymers in which the motion of chromophores is restricted. Especially, the *para*-cinnamate polymers showed indefinite stability at 80°C.³

The value of second-order NLO coefficients depends on the measurement methods and conditions, and therefore, it is of interest to determine the coefficients by a different method, in order to see if the results coincide with each other. The electroabsorption spectroscopy (EAS) is a useful tool to investigate third-order NLO properties of organic materials.^{4–6} It has been also used to determine chromophore orientation and its relaxation in polymer matrices.^{7,8} There are a few studies to determine second-order NLO coefficients by EAS, but they were determined only through second-order EAS measurements detecting the components quadratically dependent on the applied electric field, i.e., third-order NLO response.^{9–11}

Theoretically speaking, second-order NLO susceptibility $\chi^{(2)}$ can be directly determined by first-order EAS measuring a component linearly dependent on the applied electric field. In this work therefore, the second-order NLO susceptibilities of the benzoate polymers, shown in Scheme 1, were determined by the first-order EAS, and compared with values previously obtained by SHG measurements.

2. Experimental

2.1. Materials

The structures of polymers are shown in Scheme 1. They were prepared by the methods described previously.¹² The polymers had inherent viscosities of 0.3–0.4 dl/g in *N*-methylpyrrolidone (NMP) at 25°C. They were fractionated by precipitation technique from NMP/methanol, and low molecular weight portions soluble in chloroform were employed, so that they can be made into films by spin-coating from chloroform solution.

2.2. Sample preparation

The films with thickness of about 150 nm were prepared by spin-coating of their chloroform solutions (1% w/w) at 1000 rpm on ITO-coated glass at room temperature, then the films were corona-poled using a needle point cathode at a distance of 1 cm above the film surface with a voltage of 5 kV for *para*-polymer and 5.5 kV for *meta*-polymer at temperatures 10°C above their respective glass transition temperatures. After poling, semi-transparent aluminum electrodes of *ca.* 20 nm thickness were deposited by vacuum evaporation on the polymer films to construct a sandwich structure, that is shown in Fig. 1.

Linear absorption spectra of polymer samples before and after poling were measured to calculate an order parameter:

$$\phi = 1 - \frac{A}{A_0},$$

where A_0 and A , are absorbances before and after poling, respectively. Refractive index n and extinction coefficient k of the polymers were measured by a variable angle spectroscopic ellipsometer (model M-2000UI, J. A. Woollam Co., USA).

2.3. First-order EAS measurement

EAS experimental setup is schematically shown in Fig. 2. A tungsten-halogen lamp was used to provide UV-visible light. The light was monochromated and focused by the first lens on the polymer sample at normal incidence. The aluminum electrode of the sample was connected to an internal oscillator output of the lock-in

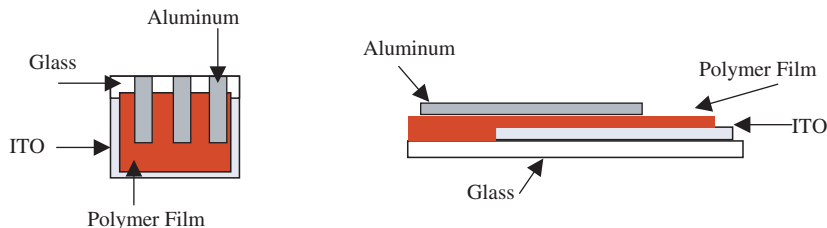


Fig. 1. Schematic sample configuration for electroabsorption measurement.

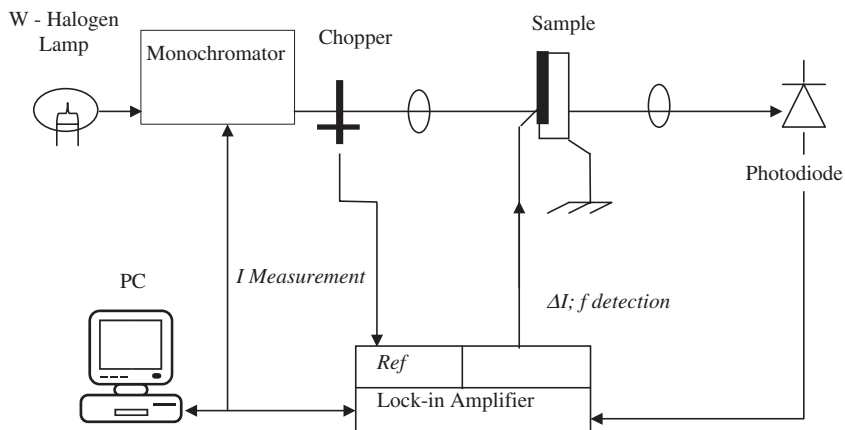


Fig. 2. Schematic diagram of electroabsorption measurement setup.

amplifier, of which amplitude and frequency were controlled by the personal computer. The ITO electrode was connected to the ground. The transmitted light was detected by the photodiode, which was connected to the computer-controlled lock-in amplifier.

The lock-in amplifier detected the component of transmitted light intensity change at the frequency f (electric field modulation frequency). This component is proportional to the applied electric field, thus the first-order EA response. The response was measured at the wavelength range of 360–800 nm. Transmission change, absorption coefficient change $\Delta\alpha$ and extinction coefficient change Δk were obtained as spectra from the response using the same procedure as the second-order EAS measurement.⁶ Refractive index change spectrum Δn was obtained from Δk by Kramers–Krönig transformation. Finally, the second-order NLO susceptibility $\chi^{(2)}$ was obtained using

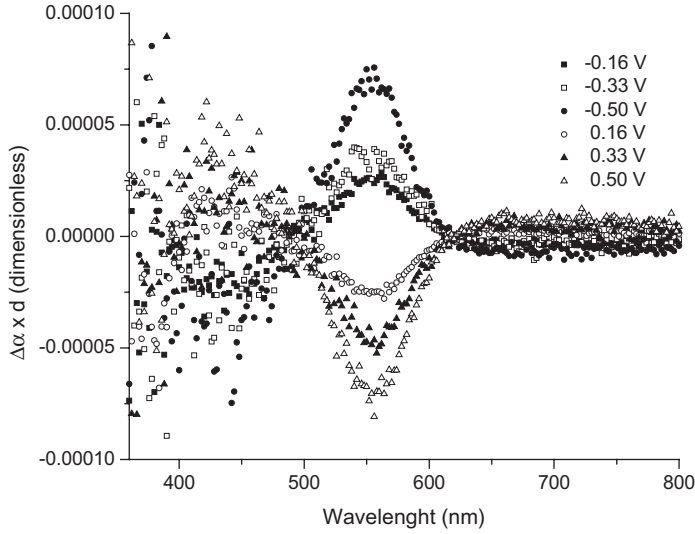
$$\operatorname{Re}(\chi^{(2)}) = \frac{n\Delta n - k\Delta k}{2\pi F},$$

$$\operatorname{Im}(\chi^{(2)}) = \frac{n\Delta n + k\Delta k}{2\pi F},$$

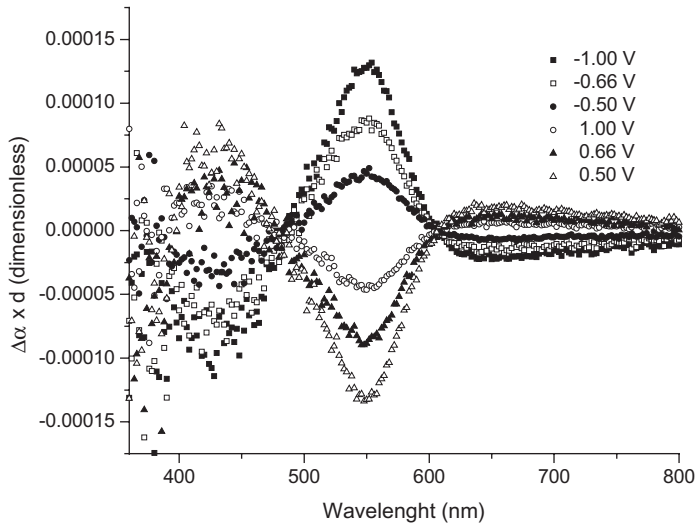
where F is the applied electric field in esu. The details of formulation will be described elsewhere.

3. Results and Discussion

According to order absorbance change, order parameters obtained by corona poling were estimated to be 0.2 for both polymers. It is known that the *meta*-polymer undergoes relaxation more quickly than the *para*-polymers.³ Therefore, the orientation parameter of the *meta*-polymer may be lower than that of the *para*-polymer at the moment of EAS measurements. Figure 3 depicts the spectra of absorption



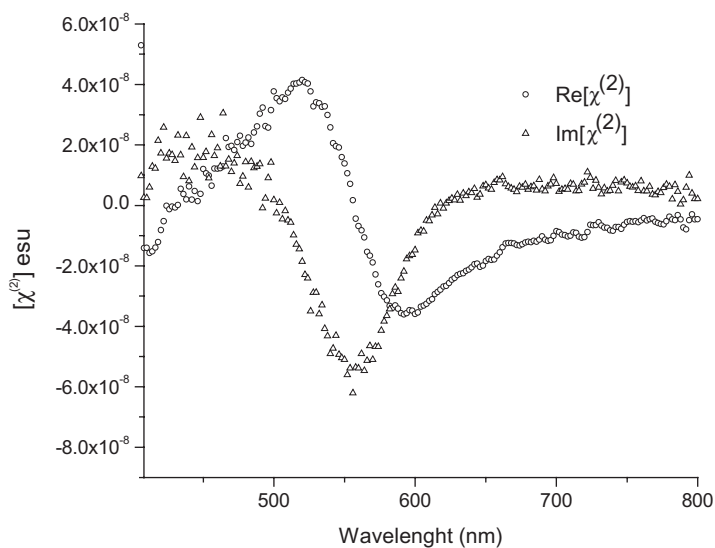
(a)



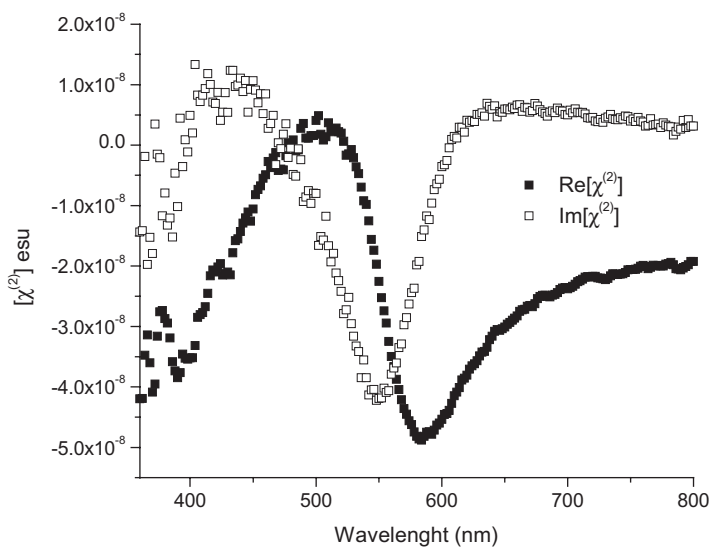
(b)

Fig. 3. Absorption coefficient change ($\Delta\alpha$) spectra of (a) *para*-polymer and (b) *meta*-polymer.

coefficient change ($\Delta\alpha$) for each polymer. A linear dependence on the applied voltage was observed, confirming that the second-order NLO response was measured. Figure 4 shows the spectra of the real and imaginary parts of $\chi^{(2)}$. For the comparison of the two polymers, the imaginary part of $\chi^{(2)}$ of each polymer is plotted in Fig. 5. The peak values of $\chi^{(2)}$ of the two polymers are summarized in Table 1. It can



(a)



(b)

Fig. 4. Real and imaginary parts of $\chi^{(2)}$ of (a) *para*-polymer and (b) *meta*-polymer.

be seen that the *para*-polymer has higher $\chi^{(2)}$ than the *meta*-polymer. The higher $\chi^{(2)}$ of the *para*-polymer is considered to be due to the linear conformation of polymer chains. The *meta*-polymer has more freedom of chain motion, and thus the relaxation takes place more readily as shown in Scheme 2.

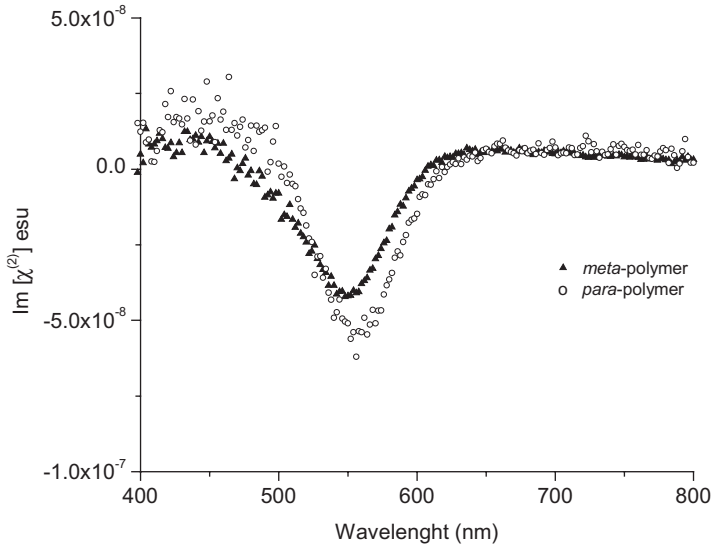


Fig. 5. Comparison of $\chi^{(2)}$ between *para*- and *meta*-polymers.

Table 1. Maximum values of $\text{Im}[\chi^{(2)}]$.

Polymer	$\text{Im}[\chi^{(2)}] \times 10^8 \text{ esu}$	$\lambda \text{ (nm)}$
<i>para</i> -	-6.20	556
<i>meta</i> -	-4.22	548

Values of SHG coefficient tensor component d_{ijk} of the *para*-polymer have been previously determined by the Maker-Fringe method²:

$$d_{31} = 32 \text{ pm/V}, \quad d_{33} = 224 \text{ pm/V}, \quad \text{at } 1064 \text{ nm.}$$

Corresponding values of d_{31} and d_{33} in esu ($1 \text{ esu} = 1 \text{ cm}^2/\text{sC}$) are

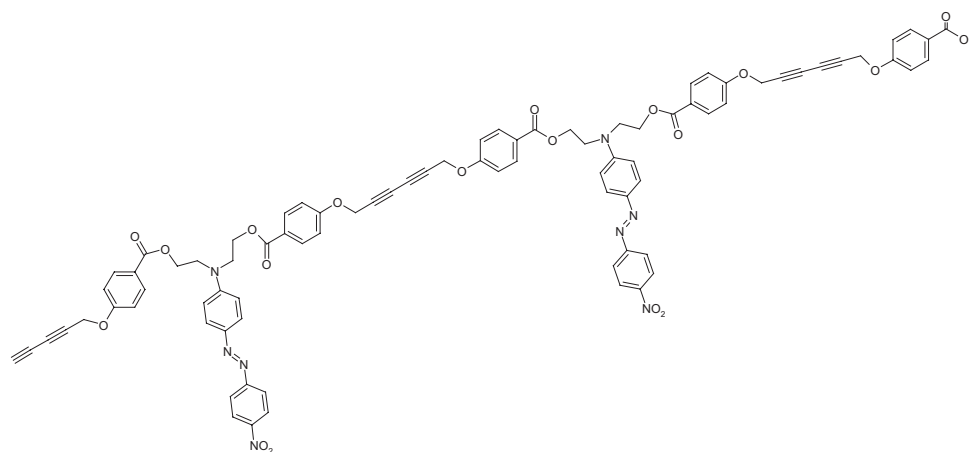
$$d_{31} = 7.6 \times 10^{-8} \text{ esu} \quad d_{33} = 5.3 \times 10^{-7} \text{ esu.}$$

Maximum value of $\chi^{(2)}$ for this polymer obtained by EAS is

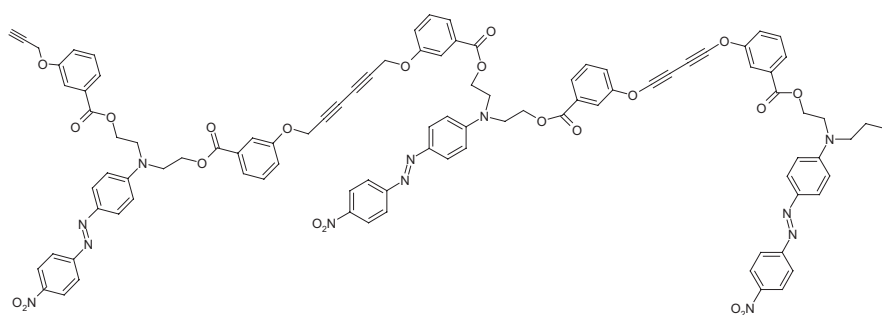
$$\text{Im}[\chi^{(2)}] = 6.2 \times 10^{-8} \text{ esu at } 556 \text{ nm.}$$

Value of d_{31} obtained by Maker-Fringe method is comparable with the value of $\text{Im}[\chi^{(2)}]$ obtained by EAS. However, some considerations must be taken into account for comparison:

(a) In our EAS measurement configuration, the obtained component is $\chi^{(2)}_{113}$ (i.e, transmitted optical field through coordinate 1, incident optical field in coordinate 1 and applied electric field in coordinate 3), so that it might be considered nearer to d_{31} value than d_{33} value, although not the same.



(a)



(b)

Scheme 2. Two-dimensional drawing of (a) poly(*para*-benzoate) and (b) poly(*meta*-benzoate) containing *Disperse Red 19*.

(b) Dispersion and resonance effects can contribute in a different way among different experimental techniques. Moreover, measurement wavelength is different in the EAS and Maker–Fringe measurements.

(c) Local field factors also differ depending on the measurements, and therefore the experimental values are always somewhat dependent on them. Taking the above considerations into account, and considering that it is known to be difficult to compare values of $\chi^{(2)}$ measured with different techniques, the values obtained by these two methods coincide considerably well. Thus, it can be said that EAS is a good experimental technique for the determination of second-order nonlinear optical susceptibilities, with the additional advantage of obtaining spectral properties.

4. Conclusion

First-order electroabsorption spectroscopy was proved to be a good alternative method for the determination of spectral second-order nonlinear optical properties of diacetylene- and dye-containing polymers. The values of nonlinear optical susceptibilities obtained here were comparable to those previously determined by the Maker-Fringe technique. It was also shown that the *para*-polymer exhibited a higher second-order nonlinear susceptibility than the *meta*-polymer, due to the more stable conformation of the former.

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