

## Third order nonlinear optical susceptibility of fluorescein-containing polymers determined by electro-absorption spectroscopy

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### ABSTRACT

Novel polymers containing xanthene groups with high dye concentrations were prepared, and their third order nonlinear optical properties were studied by electroabsorption spectroscopy technique. The polymers were amorphous with refractive indices above 1.6 in the non-resonant region. The UV–Visible absorption spectra indicate the fluoresceins molecules in the polymers are H-aggregated. They showed third order nonlinear susceptibility,  $\chi^{(3)}(-\omega:\omega,0,0)$ , of  $2.5\text{--}3.5 \times 10^{-12}$  esu.

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### 1. Introduction

Many conjugated aromatic compounds such as dyes possess interesting optical and electrical properties. Most of them do not form thin films by themselves and therefore, they are often dispersed in host polymers such as poly(methyl methacrylate) (PMMA) as composites, but miscibility is not always satisfactory and phase separation and coagulation often take place when dye concentration is increased, resulting in materials with non-homogeneous dye molecule distribution, and this is an important disadvantage for nonlinear optical (NLO) applications. Therefore, in order to achieve high functionality, it is desirable to increase dye concentration in the host polymer without phase separation and coagulation, and one of the methods is to incorporate the dye molecules into the polymer structure by chemical bonding. The present authors have previously prepared various polymers containing discrete conjugated groups such as aromatic diacetylene- and thiophene-containing polyazomethylenes [1], tolan derivatives [2], and fluorescein moieties [3]. These polymers were amorphous and soluble in organic solvents giving thin films with excellent optical quality by spin coating, for which third order NLO susceptibilities,  $\chi^{(3)}$ , of around  $10^{-10}$  esu have been observed by the DFWM technique at 532 nm.

Xanthene dyes are conjugated molecules with strong luminescence, and they have been widely investigated for several applications. Regarding NLO properties, there are many reports with Z-scan and DFWM techniques. For example, Nooraldeen et al. reported a high  $\chi^{(3)}$  of  $10^{-6}$  esu by Z-scan for Rose Bengal in dilute solutions of different solvents [4]. The second order nonlinear susceptibility of Rhodamine 6G monolayers has been reported by Leach and coworkers [5]. Ali Hassan reported the nonlinear absorption coefficient of  $10^{-4}$  cm/W for an eosin-B containing PMMA [6]. Rathnagiri Krishnamurthy et al. have reported high  $\chi^{(3)}$  values of mercurochrome dye determined by Z-scan technique [7]. Samoc and coworkers have reported NLO waveguides prepared from the phloxine B-doped polyvinylpyrrolidone [8]. Therefore, there is some interest in NLO to obtain xanthene-containing polymers with high dye concentration and excellent optical quality films. However, the homopolymerization of fluorescein-containing monomers often results in insoluble polymers [3], and in this work propargyl(3-methoxy-4-propargyloxy)cinnamate (**II**) and isophthalate with 1,6-hexanediol were chosen as comonomers to obtain soluble fluorescein-containing polymers, and electroabsorption spectroscopy (EAS) was used to evaluate the  $\chi^{(3)}$ .

EAS is a technique to measure small absorption change in a material induced by an externally applied electric field. It is a versatile and powerful tool to investigate electronic states and NLO properties of materials [9]. The experimental setup is rather simple and inexpensive, and it provides abundant information on both third and second order optical nonlinearity, polarity of electronic states, and molecular orientation. One of the most important advantages of EAS over other methods is that it does not use a laser

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but a weak monochromated light. Thus, EAS is useful to determine NLO susceptibilities for materials easily damaged by laser light. Kuzyk and coworkers have reported third order molecular susceptibilities by EAS on some dye-doped polymers [10,11]. Previously, PMMA systems containing 10% w/w of di-*n*-butyl fluorescein derivatives, were found to have  $\chi^{(3)}$  of  $10^{-12}$  esu [12,13]. In this work, novel copolymers with high xanthene concentrations were prepared and their 3-NLO susceptibilities were studied by EAS.

## 2. Experimental

### 2.1. Material

Fluorescein disodium salt, propargyl bromide (80% in toluene), 4,5'-dibromofluorescein (Dye content 95%), 3-bromo-1-propanol and 1,6-hexanediol were supplied by Aldrich Chemicals and they were used without purification. Isophthaloyl dichloride (Aldrich) was recrystallized from hexanes before use. Ferulic acid was supplied by Tsuno Rice Fine Chemicals (Japan).

### 2.2. Polymer synthesis

For polymer **1**, Scheme 1, a xanthene monomer (**I**), ether-ester-dibromofluorescein was prepared by the nucleophilic substitution of 4,5'-dibromofluorescein with 3-bromopropanol. 17 g (0.12 mol) of potassium carbonate were added to a solution of 25 g (0.05 mol) of 4,5'-dibromofluorescein in 150 ml of anhydrous *N*-methyl pyrrolidinone (NMP). The reaction mixture was stirred for 12 h at room temperature, and then 10.5 ml (0.11 mol) of 3-bromo-1-propanol were added and heated for 3 days at 80 °C. The reaction was followed by thin layer chromatography using chloroform/methanol (70/30) as eluent. The reaction was cooled down and the potassium carbonate was filtered off. The solution was then poured into large amount of water, and a coarse orange precipitate was obtained in a 70% yield. It was purified by column chromatography (silica gel; chloroform/methanol 70/30). A melting point of 160–162 °C was obtained; it was soluble in tetrahydrofuran (THF), chloroform, Dimethylformamide (DMF). UV-Vis,  $\lambda_{\text{max}}$  (DMF): 464 nm. FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3390 (—OH stretch), 2948, 2874 (—CH<sub>2</sub> stretch), 1763, 1719 (C=O stretch), 1585 (Ar C—C ring stretch). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta_{\text{H}}$ ,

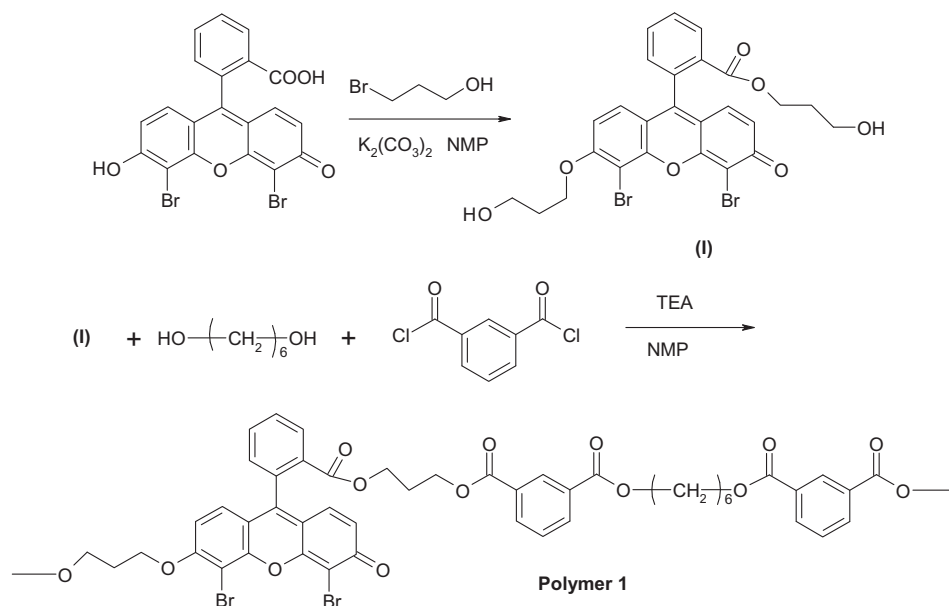
ppm): 8.28 (d, 1H, Ar-H); 7.7–7.78 (m, 2H, Ar-H); 7.34 (d, 1H, Ar-H); 7.25 (d, 1H, Ar-H); 6.95 (m, 1H, Ar-H); 6.62 (d, 1H, Ar-H); 6.84 (d, 1H, Ar-H); 4.17 (m, 4H, CH<sub>2</sub>O); 3.89 (t, 2H, CH<sub>2</sub>OH); 3.67 (t, 2H, CH<sub>2</sub>OH); 3.4 (s, 2H, OH); 2.14 (q, 2H, CH<sub>2</sub>); 1.87 (q, 2H, CH<sub>2</sub>). Anal. calcd. for C<sub>26</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>7</sub> (%): C, 51.51; H, 3.66. Found: C, 53.28; H, 3.67.

The polymer **1** was prepared by polycondensation. 2 g (0.003 mol) of (**I**), 0.39 g (0.003 mol) of hexan-1,6-diol and 0.35 ml of dry triethylamine were dissolved in 12 ml of anhydrous NMP, and 1.31 g (0.006 mol) of pure isophthaloyl dichloride were added at room temperature, and the mixture was stirred for 24 h. The reaction system was poured into 1 l of water, and the precipitated polymer was filtered, and dried in vacuum. The polymer **1** was purified by reprecipitation from its chloroform solution with methanol. Bromine analysis: 15.6% (calcd. 16.2%). *T*<sub>g</sub>: 117 °C (by thermomechanical analysis). Inherent viscosity: 0.20 dl/g in DMF at 25 °C. The dye content is 60% w/w. FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2944, 2852 (—CH<sub>2</sub> stretch), 1749, 1718 (O=C=O stretch), 1594 (Ar C—C ring stretch).

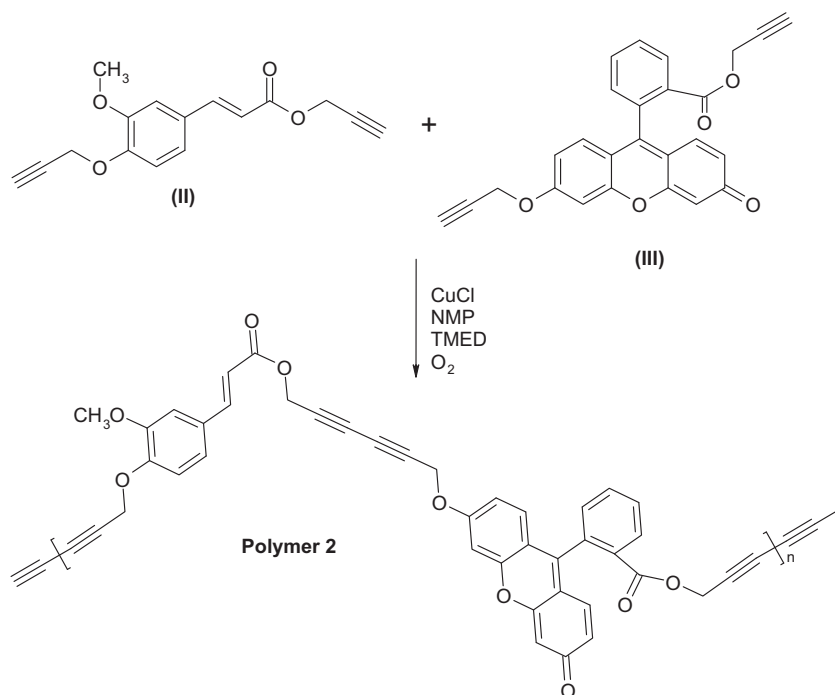
The polymer **2**, Scheme 2, was prepared from the oxidative coupling copolymerization of the two bisacetylenic monomers (**II**) and (**III**), which were prepared by the previously reported methods [14,3]. 0.5 g (0.0012 mol) of (**III**) and 0.6 g (0.0022 mol) of (**II**) were dissolved in 5 ml of NMP, and 0.05 g of CuCl and 0.3 ml of *N,N,N',N'*-tetramethylethylenediamine (TMED) were added. The system was stirred at 55 °C for 27 h under flow of oxygen. The system was poured into methanol, and the yellow precipitated polymer was filtered off, washed with methanol and dried under vacuum. Yield was quantitative. *T*<sub>g</sub>: 133 °C (by thermomechanical analysis); inherent viscosity: 0.5 dl/g in DMF at room temperature. The polymer contains 45% w/w of fluorescein. It was readily soluble in a variety of organic solvents, chloroform, DMF, NMP. FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2931, 2851 (—CH<sub>2</sub> stretch), 1714 (O=C=O stretch), 1632 (C=C stretch), 1596 (Ar C—C ring stretch).

### 2.3. Characterization

<sup>1</sup>H NMR spectra were taken using a Bruker Avance 400 MHz spectrometer, and FT-IR spectra were taken using Thermo Scientific spectrophotometer model Nicolet 6700. UV-Visible spectra were recorded by a Varian Cary 400 UV-Vis spectrophotometer,



Scheme 1. Synthesis of polymer 1.



Scheme 2. Synthesis of polymer 2.

the concentration of each solution was around  $10^{-4}$  M. The inherent viscosity was determined in DMF solution at 25 °C using an Ubbelohde viscosimeter. The Bromine elemental analysis of polymer 1 was done by Columbian Analytical Services Laboratory of Tucson Az. USA. Differential scanning calorimetry was performed using a TA Instrument Model 2100 with a heating rate of 10 °C/min under nitrogen atmosphere. X-ray diffractometry was carried out using a Siemens D-500 diffractometer  $\text{CuK}\alpha_1$  radiation of 1.540 Å, which proved that the polymers were amorphous.

#### 2.4. EAS

For the EAS measurements, sandwich-structured samples were fabricated as follows. The polymers were dissolved in DMF and spin-coated on ITO coated glass substrates at 70 °C. The film thickness was determined to be 118 nm by a spectroscopic ellipsometer (M-2000UI, J.A. Woollam, Co.), together with refractive index and extinction coefficient spectra. Finally, semitransparent Al electrodes of 27 nm thickness were fabricated by vacuum deposition.

The  $\chi^{(3)}$  was measured by the second order electroabsorption technique. Schematic diagram of the experimental setup is shown in Fig. 1. White light from a tungsten-halogen lamp was monochromated by a computer-controlled grating type monochromator (CT-25GD, JASCO, Co.) and focused onto a sample. The transmitted light was collimated to be detected by a Si photodiode. AC electric field at the frequency of  $f = 137.5$  Hz was applied to the sample, and a very small change in absorption was detected as the change in photocurrent synchronized to the applied electric field by a lock-in amplifier (SR830, Stanford Research, Inc.). The measurements were performed at voltages varying from 1 to 5 V. The  $2f$  component was detected to extract the absorption change quadratic to the applied field, which corresponds to the third order NLO response. By scanning the wavelength of the monochromator, the spectrum of absorption change was obtained. Real and imaginary part of  $\chi^{(3)}$  was calculated from the spectra using the procedure described in the literature [13].

### 3. Results and discussion

The visible absorption spectra of xanthene dyes are rather complicated due to aggregation of dye molecules, and visible absorption spectra change depending on solvents and concentration [15–17]. Fig. 2 shows the visible absorption spectra of dibromofluorescein, the monomer I and Polymer 1 in DMF solutions. The absorption spectrum of dibromofluorescein in DMF (A) showed the typical absorption peak at 538 nm, which corresponds to the monoanionic species formed by the interaction of the phenolic proton with DMF. When the phenolic hydrogen is substituted with 3-hydroxypropyl group, this absorption at 538 nm disappears, as there is no longer resonance structure, giving a typical spectrum of substituted fluoresceins (B). The spectrum of the polymer (C) was similar to that of the monomer, although a small shoulder was observed at 540 nm. Fig. 3 shows the absorption spectra of spin coated film and the DMF and THF solutions of polymer 1. The shoulder at 540 nm disappeared for the THF solution. The polymer is very soluble in DMF and not so soluble in THF. In fact the THF solution is yellowish orange and the DMF solution is reddish. This is because the polymer molecules are solvated by DMF and are tangled in THF. Therefore, a small red shift in DMF is observed, and the shoulder can be due to the solvation of DMF to the quinolic part of the dye. It is known that xanthene dyes exist as H-aggregates [16,17], as many other polar dyes [18], and it seems that solvation influence the magnitude of aggregation. The visible spectrum of the polymer film shifted to red due to higher refractive index of the polymer matrix than that of the solutions. The shoulder at 540 nm for the DMF solution no longer existed as there was no DMF in the film.

Fig. 4 shows visible absorption spectra of polymer 2. The shapes of spectra are similar each other in the solid film or solution. In the case of the film prepared by spin coating from dichloromethane, some bathochromic shift was also observed. For the spectra in solution, there was no significant difference between the THF and DMF, although a slight red shift was observed for the DMF as in the case of polymer 1. The polymer chain is more tangled in THF than in DMF, and the dye molecules are more closely

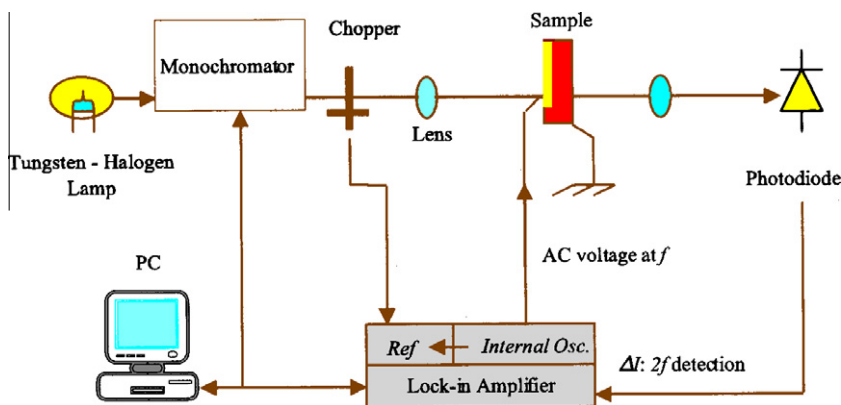


Fig. 1. Schematic diagram of EAS set-up.

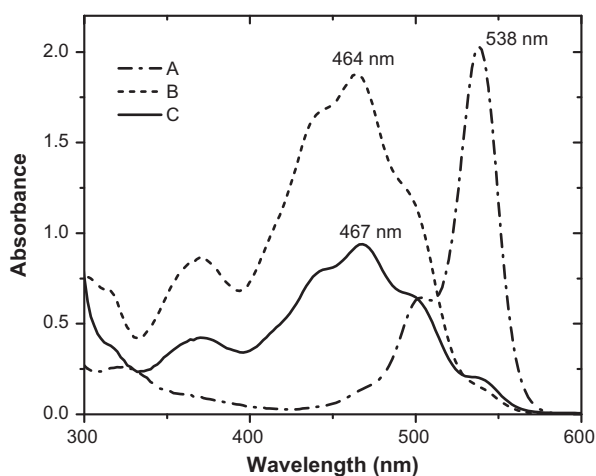


Fig. 2. Visible absorption spectra of dibromofluorescein (A); monomer (B); and polymer 1 (C) in DMF. Concentration:  $1 \times 10^{-4}$  M.

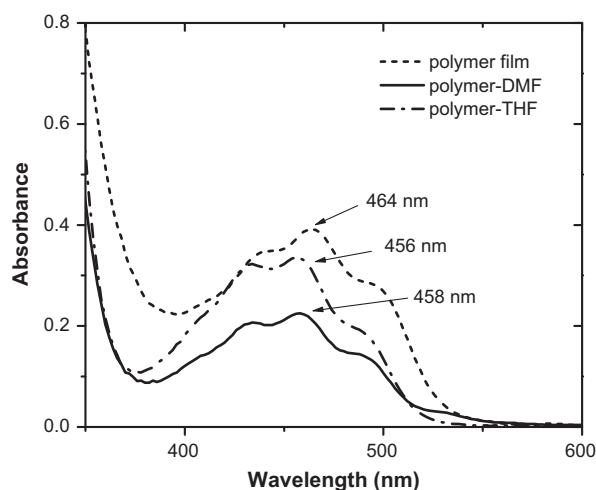


Fig. 4. UV-Visible absorption spectra of polymer 2.

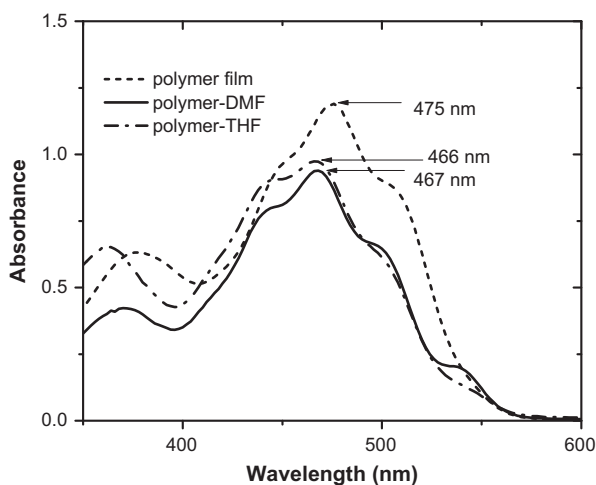


Fig. 3. UV-Visible absorption spectra of polymer 1.

aggregated. The THF solution is yellowish while the DMF solution is orange.

The evaluated  $\chi^{(3)}$  spectra of polymers 1 and 2 are shown in Figs. 5 and 6, respectively. The  $\chi^{(3)}$  values were taken from the maximum peaks of imaginary part because they are derived from

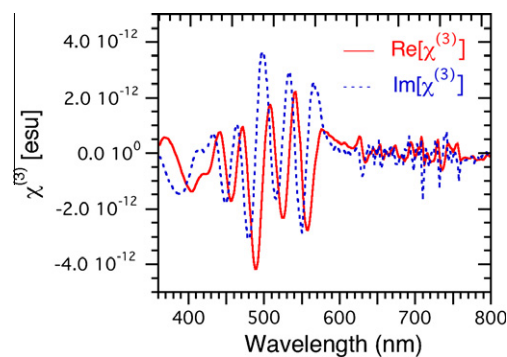


Fig. 5.  $\chi^{(3)}$  Spectra of polymer 1 obtained by EAS.

the experimental data. The real values contain some ambiguity originating from Kramers–Kronig transformation, and the real part can have some offset (constant shift of the value) depending on the wavelength range for transformation. Polymer 1 presented a maximum imaginary peak  $\chi^{(3)}$  of  $3.5 \times 10^{-12}$  esu, while polymer 2 showed a maximum peak of  $2.5 \times 10^{-12}$  esu. The  $\chi^{(3)}$  of dipropargyloxyfluorescein monomer (III) of Scheme 2, dispersed in PMMA by 1% w/w, was also determined, and it was found to be only  $0.04 \times 10^{-12}$  esu. Enhancement of  $\chi^{(3)}$  nearly two order of magnitude is consistent with the fact that the polymer contained 45% w/w of dye units, indicating that the dye concentration is an

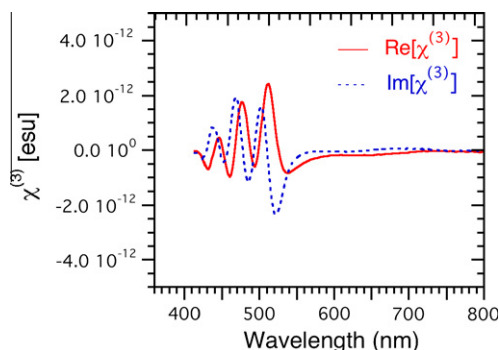


Fig. 6.  $\chi^{(3)}$  Spectra of polymer **2** obtained by EAS.

important factor for  $\chi^{(3)}$ . Polymer **1** contained 60% w/w dye, and it showed even higher  $\chi^{(3)}$  value of  $3.5 \times 10^{-12}$  esu. Previously the  $\chi^{(3)}$  of various dibutylfluoresceins such as of phloxine and eosin, dispersed in PMMA by 10% w/w, were determined to be on the order of  $10^{-13}$  esu [12,13]. In this case also increase in the dye concentration significantly enhanced the  $\chi^{(3)}$  values. These  $\chi^{(3)}$  values of these polymers represent those of H-aggregated xanthene dyes. The fluorescein dyes in these studies have neither phenolic protons nor metal phenolate and there is no dissociation to form ionic structures, and therefore the 3-NLO properties are only from electronic contribution.

It seems that EAS technique gives  $\chi^{(3)}$  values numerically lower than those determined by other methods using a laser, such as Z-scan and DFWM techniques. For example, the  $\chi^{(3)}$  value of oligodiphenylbutadiyne was found to be on the order of  $10^{-12}$  esu by EAS, while the  $\chi^{(3)}$  was determined to be  $5.9 \times 10^{-10}$  esu by the close aperture Z-scan technique with 25 ps laser pulse at wavelength 1064 nm [19]. A polymer containing 57% w/w of the propargylfluorescein (**III**) in its main chain showed a  $\chi^{(3)}$  value of  $3 \times 10^{-10}$  esu by the DFWM technique with a ps laser at 532 nm [3], while the Polymer **2** having the same dye unit (**III**) showed a  $\chi^{(3)}$  of  $2.5 \times 10^{-12}$  esu by EAS. Narayana Rao and coworkers have discussed the  $\chi^{(3)}$  values obtained by EAS and FWM experiments for a butadiene-linked porphyrin polymer [9]. Rau et al. [20] also have mentioned significant differences up to 14 times in  $\chi^{(3)}$  determined by Z-scan and third harmonic generation (THG) for various organic solvents. In any third order NLO measurement using a laser such as Z-scan, THG, and DFWM processes, three optical electric fields interact to induce the nonlinear polarization, while in EAS one field is the weak monochromated light and the other two fields are the externally applied low-frequency electric field. Therefore, the influence of resonance effect is significantly different between the former three methods and EAS.

The Z-scan experiment was also carried out for the spin-coated films for comparison with EAS technique, using a pulsed Nd-YAG laser (26 ps) at 532 nm. However, the  $\chi^{(3)}$  could not be obtained due to rapid degradation of the films by the laser. The results demonstrate the advantage of EAS in terms of significantly lower damage in the sample during measurement.

## 4. Conclusion

New polymers containing high xanthene dye concentrations were prepared and their  $\chi^{(3)}$  were determined by EAS. According to the UV-Visible absorption spectra, the dye molecules in the polymers are considered to exist as H-aggregates. The  $\chi^{(3)}$  values of the polymers **1** and **2** were found to be  $3.5$  and  $2.5 \times 10^{-12}$  esu, respectively. The concentration of dye is an important factor for the bulk  $\chi^{(3)}$  values, and our polymers showed significant enhancement in  $\chi^{(3)}$  compared with guest–host materials. The magnitude of  $\chi^{(3)}$  by the EAS is about two orders less than that obtained by other methods.

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