

Second-order Nonlinear Optical Properties of Amorphous Molecules Based on 5-(4-Diethylamino-benzylidene)-1,3-dimethyl-pyrimidine-2,4,6-trione

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Two coupled molecules were successfully synthesized by condensation of amine-donor-substituted barbituric acid derivatives as nonlinear optical chromophores. A flexible spacer of the alkyl chain with different lengths of carbon chains (5 and 6 carbons) was introduced between two chromophores, which prevented crystallization and aggregation of molecules. Two coupled molecules (B-Cn-B, n=5, 6) had glass-transition temperatures on a second heating around 81 and 76°C without melting points, respectively. To explore the linear optical properties, thin-films were prepared and examined by a photometry method using Nd:YVO₄ CW laser. Also, microscopic and macroscopic nonlinear optical properties were measured by Hyper-Rayleigh Scattering (HRS) and the Maker Fringes method using Nd:YAG ps pulse laser, respectively. In spite of the moderate hyperpolarizabilities of coupled molecules, the second order NLO coefficient (d_{33}) was larger than the conventional Disperse Red 1 doped PMMA polymeric system.

key words: Nonlinear optical, electro-optical, amorphous molecules, chromophores, dimethylbarbituric acid

INTRODUCTION

Over the past decade, a great deal of research has been focused on the development of nonlinear optical (NLO) and electro-optic (EO) materials because of their potential in various applications such as information storage, optical switching, and signal processing [1,2]. The most famous nonlinear optical material would be an inorganic crystal, such as lithium niobate. Many organic chemists, however, have attempted to substitute the expensive inorganic crystals with low-cost organic materials, e.g., chromophore/polymer composite system or polymeric system with side-chain NLO chromophores [3]. The advantages of NLO polymers compared to inorganic crystals include easier fabrication of optical wave-guides on device substrate, lower dielectric constants, and potentially higher NLO susceptibility, etc. Second order NLO susceptibilities could be enhanced by development of highly active organic π -conjugated chromophores containing various electron donor and acceptor groups [4].

Most of the NLO chromophores were crystalline molecules. Therefore, they often lacked the device stability arising from the limited compatibility between nonpolar polymer matrix and polar NLO chromophore. The phase separation of the composites seriously limited the optimization of nonlinear optic properties and lifetime of the

materials. From these reasons, the glassy and amorphous molecules have been developing for many desirable properties such as transparency, low crystallization and facile fabrication [5]. An important aspect of amorphous NLO molecules was to improve the long-term stability, to increase NLO molecule content of the device, and to minimize the phase separation in the device comparing with the crystalline molecules.

In this study, two amorphous coupled-molecules were synthesized based on the following nonlinear optical chromophore, 5-(4-diethylamino-benzylidene)-1,3-dimethyl-pyrimidine-2,4,6-trione. A flexible spacer of the alkyl chain with different lengths (5 and 6 carbons) was introduced between two electro-optical chromophore units, which prevented crystallization of molecules. To characterize the linear optical property of the molecule, a thin-film was prepared and examined by a photometry method using Nd:YVO₄ CW laser. Also, the first order hyperpolarizability, β , and the second order nonlinear optical coefficient, d_{33} , have been determined by Hyper-Rayleigh Scattering (HRS) and Maker Fringe technique, respectively [6-9].

MATERIALS AND METHODS

Characterization and Sample Preparation

¹H-NMR spectra were taken by Varian Unityplus NMR Spectroscopy 300 MHz. The UV-Vis absorption spectra were recorded using a Hewlett-Packard 8453A spectrophotometer. The glass transition temperatures (T_g) were determined with a differential scanning calorimeter (DSC), Perkin-Elmer Pyris 1

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series at a heating rate of 10 °C/min under nitrogen atmosphere. Film thickness, refractive indices and extinction coefficients (at fundamental and doubling wavelength) were determined by a photometry method using Nd:YVO₄ CW laser [10].

Films were prepared with spin-coating of the solution at a rotation speed of 2000 rpm, consisting of 5 wt% in 1,1,2,2-tetrachloroethane. Each sample was filtered with 0.45 μm Teflon filter (Whatman) to remove possible small dusts and undissolved particles before spin-coating. These films were subsequently dried in an oven at 50 °C for 24 hours to remove the residual solvent.

Materials

4-(Diethylamino)salicylaldehyde, potassium hydroxide, Aliquat[®]336, and 1,1-diphenylhydrazine hydrochloride were purchased from Aldrich Chemical Co. 1,5-Dibromopentane and 1,6-dibromohexane were purchased from Merk-Schuchardt. 1,3-Dimethylbarbituric acid purchased from Tokyo Kansei Kogyo Co. Ltd was used without further purification.

Synthesis of 4-(diethylamino)-2-((6-[5-(diethylamino)-2-formylphenoxy]pentyl)oxy)benzaldehyde (C5)

In a 2 L three-necked flask equipped with a magnetic stirrer and a reflux condenser, 75 g (0.388 mol) of 4-(Diethylamino)salicylaldehyde, 500 mL of tetrahydrofuran (THF), 53.6 g (0.388 mol) of potassium hydroxide, and several drops of Aliquat[®]336 were added and stirred at 100°C. 1,5-Dibromopentane (45 g/0.194 mol) was slowly dropped into the mixture. This mixture was reacted at reflux for 24 hours and then the cooled mixture was poured into 3 L of cold water. The precipitate was filtered, dried, and purified two times by crystallization from ethyl acetate to give 84 g (95% yield) of a desired product as yellow powder (mp 123°C): ¹H-NMR (CDCl₃); δ(ppm) 10.18 (2H, s), 7.72 (2H, d), 6.28 (2H, d), 6.03 (2H, s), 4.07 (4H, t), 3.43 (8H, m), 1.94 (4H, m), 1.73 (2H, m), 1.22 (12H, t).

Synthesis of 4-(diethylamino)-2-((6-[5-(diethylamino)-2-formylphenoxy]hexyl)oxy)benzaldehyde (C6)

The synthetic procedures (C6) were used as the same method as in C5. 94 % yield, mp 155°C: ¹H-NMR (CDCl₃); δ(ppm) 10.19 (2H, s), 7.72 (2H, d), 6.28 (2H, d), 6.02 (2H, s), 4.06 (4H, t), 3.43 (8H, m), 1.86 (4H, m), 1.58 (4H, m), 1.22 (12H, t).

Synthesis of 5-((4-(diethylamino)-2-((5-[5-(diethylamino)-2-((1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)methyl)phenoxy]pentyl)oxy)phenyl)methylene)-1,3-dimethylhexahydro-2,4,6-pyrimidinetrione (B-C5-B)

Into a stirred solution of 1,3-dimethylbarbituric acid (0.733 g, 4.69 mmol) in 100 mL of ethanol was added C5 (1.00 g, 2.13 mmol) in 100 mL of ethanol and stirring was maintained for 7 hours at 80°C. The mixture was filtered and then the precipitation was purified by recrystallization with tetrahydrofuran. The product was obtained as dark-yellow powder (0.97 g, 62 %

yield), mp 185°C: ¹H-NMR (CDCl₃); δ (ppm) 9.04 (2H, s), 8.92~8.89 (2H, d), 6.32~6.28 (2H, d), 6.00 (2H, s), 4.11~4.07 (4H, t), 3.49~3.42 (8H, m), 3.35~3.33 (12H, m), 2.02~1.95 (4H, m), 1.81~1.79 (2H, m), 1.25~1.20 (12H, m).

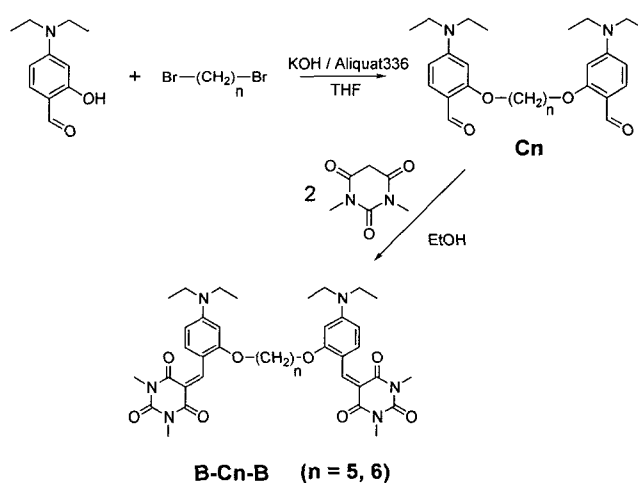
Synthesis of 5-((4-(diethylamino)-2-((5-[5-(diethylamino)-2-((1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)methyl)phenoxy]hexyl)oxy)phenyl)methylene)-1,3-dimethylhexahydro-2,4,6-pyrimidinetrione (B-C6-B)

The synthetic procedures were used as the same method as in B-C5-B. 53 % yield, mp 201°C: ¹H-NMR (CDCl₃); δ (ppm) 7.95 (2H, d), 7.61 (2H, s), 7.40~7.05 (20H, m), 6.40 (2H, d), 6.11 (2H, s) 3.85 (4H, t), 3.38 (8H, m), 1.55 (4H, m), 1.20 (14H, m).

RESULT AND DISCUSSION

We synthesized amorphous molecules coupled with two nonlinear optic chromophore units in order to improve the phase stability and prevent crystallization and aggregation of molecules. Simple amine-donor-substituted barbituric acid derivative chromophores have been already well studied as a nonlinear optical chromophore with large hyperpolarizability together with good thermal stability [11]. As shown in Scheme 1, the coupled dialdehyde C_n (n=5 and 6) was readily synthesized by condensation of 4-(diethylamino)salicylaldehyde with dibromoalkylenes using potassium hydroxide as a base. The coupled molecules (B-C_n-B) with different lengths of carbon chains (5 and 6 carbons) were successfully synthesized by Knoevenagel condensation [18]. As shown in Figure 1, the chemical structures of the amorphous molecules, B-C5-B and B-C6-B were confirmed by ¹H-NMR spectroscopy. The chemical shifts of aliphatic protons could be identified at 1.99 ppm and 1.79.

As shown in Figure 2, for a film prepared from spin-coating, UV-visible spectra of B-C6-B exhibited the usual absorption band with a maximum absorption of 473 nm. After corona poling, the absorbance decreased due to the alignment



Scheme 1. Synthesis of amorphous molecule, B-C5-B and B-C6-B.

of the dipole moments of the chromophores [Figure 2 (b)]. The linear order parameter was deduced from absorption spectra using the following equation:

$$\Phi = \{3(\cos^2\theta) - 1\}/2 = 1 - A_p/A_o$$

where θ is the angle between the dipole moment of the chromophore and the normal to the sample plane, A_o and A_p are the absorbance before and after poling, respectively. The order parameter was 0.15 after poling and did not decrease seriously after a day [Figure 2 (c)].

Table 1 summarized the optical and thermal properties of

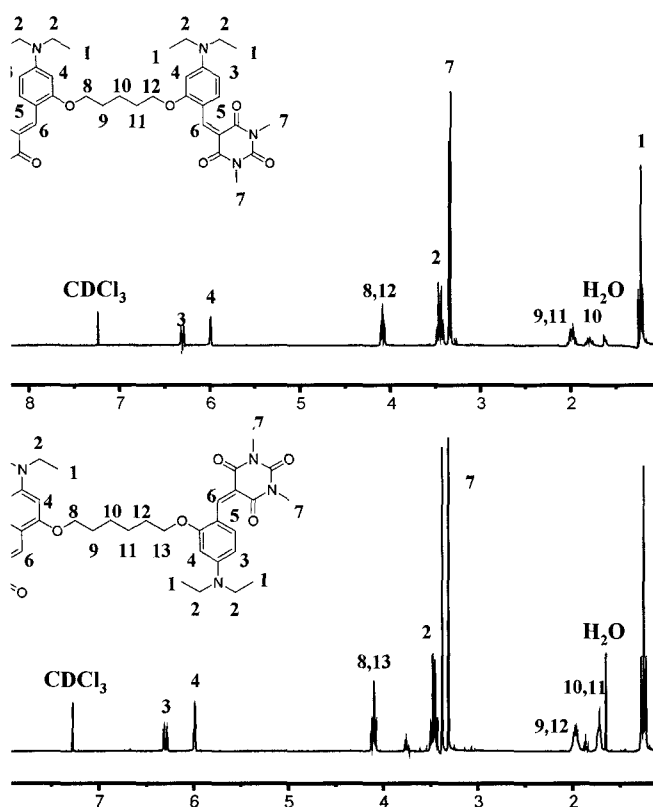


Figure 1. $^1\text{H-NMR}$ spectra of the amorphous molecules; (a) B-C5-B and (b) B-C6-B.

the chromophores. All coupled molecules (B-Cn-B) had melting points around 185 and 201°C at first heating. However, only the glass-transition temperature (T_g) at second heating was determined to be around 81 and 76°C without melting points. This observation indicated that these molecules were amorphous molecules that formed stable glass-phases, i.e., no recrystallization occurred upon cooling at 10°C/min. In order to have a second-order nonlinearity, electric field-induced corona poling was used to orient the NLO chromophores. Poling could be performed above T_g during approximately 15 min.

The hyperpolarizability is generally described by the two level model as shown on following equation [12].

$$\beta = \frac{3e^2\eta^2}{2m} \frac{\Delta\mu_{eg}E_{eg}f}{(E_{eg}^2 - E^2)(E_{eg}^2 - 4E^2)}$$

where $\Delta\mu_{eg}$ is the change of dipole moments between ground and excited states, E_{eg} is the excitation energy from the ground state to the first excited state and f is the oscillator strength of the transition from the ground state to the first excited state.

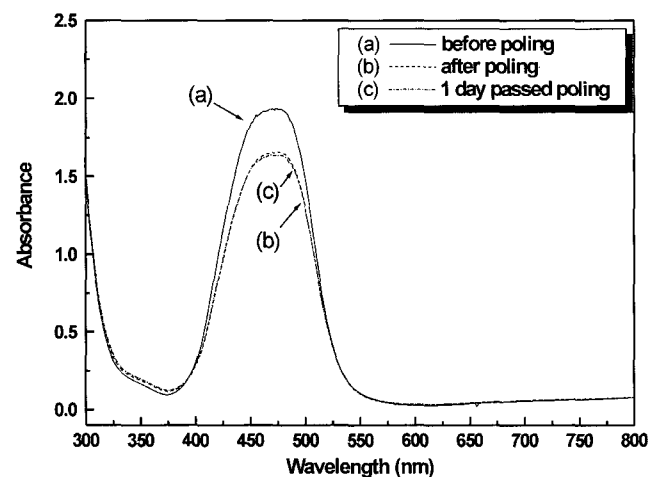


Figure 2. Absorbance spectra of a B-C6-B film: (a) before poling; (b) shortly after poling; (c) 1 day after poling; showing the relaxation of the poling-induced alignment.

Table 1. Optical and thermal properties of coupled NLO molecules.

	Refractive Index ^{a)}		Extinction coefficient ^{a)}		$\lambda_{\text{max}}^{\text{b)}$ (nm)	T_m (°C) ^{c)}	T_g (°C) ^{d)}
	1064 nm	532 nm	1064 nm	532 nm			
B-C5-B	1.80	2.05	0.01	0.09	473	185	81
B-C6-B	1.74	2.04	0.02	0.08	473	201	76

^{a)}Refractive index and extinction coefficients (at fundamental and doubling wavelength) were determined by a photometry method using Nd:YVO₄ cw laser.

^{b)}The UV-vis absorption spectra were recorded using a Hewlett-Packard 8453A spectrophotometer.

^{c)}The melting points (T_m) at first heating were determined with a differential scanning calorimeter (DSC), at a heating rate of 10°C/min under nitrogen atmosphere.

^{d)}The glass transition temperatures (T_g) at second heating were determined with a differential scanning calorimeter (DSC), at a heating rate of 10°C/min under nitrogen atmosphere.

For a binary system consisting of a chromophore dissolved in a solvent, in the very dilute concentration limit, the intensity of the second harmonic light $I_{2\omega}$ can be following equation [6,7,13]

$$I_{2\omega} = G(N_s\beta_s^2 + N_c\beta_c^2)e^{-(2\sigma_{\omega^1} + \sigma_{2\omega^2})N}I_{\omega}^2$$

where N_s and N_c represent the number densities of the solvent β_s^2 and β_c^2 the concentration of chromophore, respectively. and are the effective first hyperpolarizabilities of solvent and chromophore and σ_{ω} and $\sigma_{2\omega}$ are the absorption cross-section of fundamental frequency and doubling frequency. G is proportionality constant depending on the scattering geometry and the solvent environment of the chromophore.

For our HRS experiment, we chose para-nitroaniline in chloroform as an external reference method with Beer's Law correction. The first order hyperpolarizability (β) of B-C5-B and B-C6-B used in Hyper-Rayleigh Scattering (HRS) experiment were measured to be $(31.7\pm 4)\times 10^{-30}$ esu and $(32.1\pm 4)\times 10^{-30}$ esu, respectively. The results are summarized in Table 2.

Second Harmonic Generation measurements of nonlinear optical materials (eg. conventional inorganic materials, poled polymer) were carried out by using Maker fringes produced from a quartz crystal reference. An Y-cut quartz crystal (3 mm thickness, $d_{11}=0.3$ pm/V) was used as a reference for determining the relative intensity of the SH signals generated from the samples.

The second harmonic coefficients, d_{33} and d_{31} , can be obtained from the reference normalized second harmonic intensity ($I_{2\omega}$), and is described by

$$\frac{I_{2\omega}(2\omega)}{I_{\omega}^2(\omega)} = \frac{cn_1}{2\pi} \left(\frac{2\pi}{cn_{\omega}} \right)^2 \frac{16\pi^2 |d_{eff}(\beta)|^2}{(n_{\omega}^2 - n_{2\omega}^2)^2} 4r_{\alpha}^4 G^{\alpha} \sin^2 \Psi$$

$$\Psi = \frac{2\pi}{\lambda} L(n_{\omega} \cos \phi_1 - n_{2\omega} \cos \phi_2)$$

where I_{ω} is the intensity of fundamental wave, n_{ω} , $n_{2\omega}$, ϕ_1 , and ϕ_2 are the refractive indices and the refraction angles at ω and 2ω respectively. L is the thickness of material and d_{eff} is the effective nonlinear optical coefficient.

The effective Second Harmonic coefficient, $d_{eff}(1/2\chi_{eff})$ depends on the input and output polarizations of the light used in the Maker Fringes experiments as well as the orientation of the sample relative to the plane of incidence. The coefficient, d_{33} is described by [14,15]

$$d_{33} = N_{film}^{eff} \cdot \beta \cdot f_z^2(\omega) \cdot f_z(2\omega) \cdot \langle \cos^2 \delta \rangle$$

$$d_{31} = N_{film}^{eff} \cdot \beta \cdot f_z^2(\omega) \cdot f_z(2\omega) \cdot \langle \frac{\cos \delta \cdot \sin^2 \delta}{2} \rangle$$

where N_{film}^{eff} eff is the effective chromophore number density, δ is the polar angle, and is local field factor. The ratio of nonlinear coefficients of poled polymeric system was

known as $d_{33} \approx 3d_{31}$ in the limit of low poling field. [1]

The laser light was generated by a mode-locked Nd:YAG laser (10 Hz, 40 ps pulse width) at a fundamental wavelength of 1.064 μ m. A photo-multiplier tube (PMT; Hamamatsu R955) was used as an emergent incoherent or coherent SHG light and the optical signal is compensated against p -NA and quartz crystal reference.

We measured SHG intensity as a function of incident angle for B-C5-B and B-C6-B, and the results were shown in Figure 3. The open circles/squares are experimental data, and the solid curves are theoretical fitting curves. A beam splitter and a photodiode were used to compensate the intensity fluctuations of the fundamental beam (1064 nm), the output signals from the photodiode and PMT were detected using a peak detector.

In spite of the moderate hyperpolarizabilities of B-C5-B and B-C6-B, the second order NLO coefficient, d_{33} was larger than the conventional Disperse Red 1 (DR1) doped PMMA polymeric system [16,17]. These results were due to the effects that flexible molecules could be easily orientated and composed of different chromophore contents comparison with DR1/PMMA system. The results are summarized in Table 2.

As shown in Figure 4, we also investigated the thermal relaxation stability of the films by normalized SHG signal as

Table 2. Nonlinear optical properties of coupled NLO molecules.

	β [10^{-30} esu] ^{a)}	d [10^{-8} esu] ^{b)}	Ratio
B-C5-B	31.7 \pm 4	$d_{33} = 8.3\pm 0.3$ $d_{31} = 6.4\pm 0.2$	$d_{33}/d_{31} = 1.30$
B-C6-B	32.1 \pm 4	$d_{33} = 9.4\pm 0.3$ $d_{31} = 7.7\pm 0.3$	$d_{33}/d_{31} = 1.22$

^{a)}The first order hyperpolarizability (β) of the molecules was measured by Hyper-Rayleigh Scattering Method.

^{b)}Second Harmonic Generation measurements of the nonlinear optical materials were carried out by using Maker fringes technique.

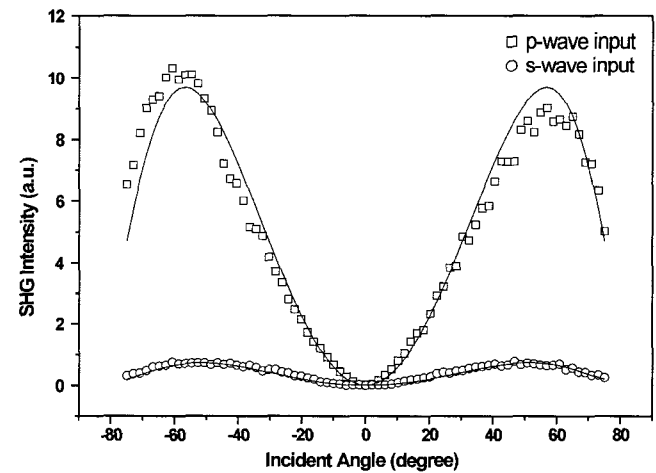


Figure 3. Angular dependence of SHG signal in a poled B-C6-B film.

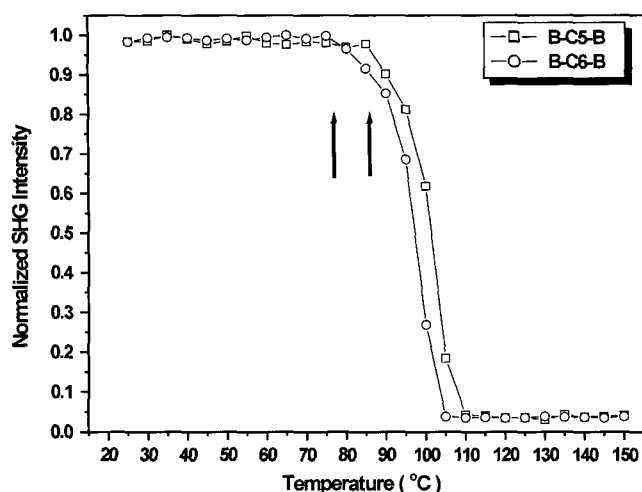


Figure 4. Thermal stability of SHG intensity as a function of ramping temperature.

a function of ramping temperature at a heating rate of 2°C/min. The glass transition temperature of the sample was consistent with the decreased temperature point, suggesting a direct method of the glass transition temperature measurement for monolithic materials. These amorphous molecules are potential NLO chromophores for polymeric photorefractive application due to their low glass-transition temperatures.

CONCLUSIONS

We synthesized two amorphous coupled-molecules based on a nonlinear optical chromophore, 5-(4-diethylamino-benzylidene)-1,3-dimethyl-pyrimidine-2,4,6-trione. A flexible spacer of the alkyl chain containing ether linkage was introduced between two electro-optical chromophore moieties, which minimized the phase separation in the device. The coupled molecules had only glass-transition temperatures on a second heating without melting points. The first order hyperpolarizability (β) were measured by Hyper-Rayleigh Scattering (HRS) experiment. In spite of the moderate hyperpolarizabilities, the second order NLO coefficient (d_{33}) was larger than the conventional DRI doped PMMA polymeric system. Now, we are investigating the optimization of chromophore content by using this amorphous chromophore in guest-host polymeric system.

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REFERENCES

1. Prasad, P. N. and D. J. Williams (1991) Introduction to

Nonlinear Optical Effects in Molecules and Polymers; John Wiley & Sons, Inc: New York. pp 132-174

- Bosshard, Ch., Bosch, M., Liakatas, I., Jagar, M., and Gunter, P. (1994) *Nonlinear Optical Effects and Materials*; Gunter, P. Ed., *Springer series in optical sciences*. pp163-299
- Burland, D. M., R. D. Miller, and C. A. Walsh (1994) Second-order nonlinearity in poled-polymer systems, *Chem. Rev.* **94**, 31
- Marder, S. R., B. Kippelen, A. K. Y. Jen, and N. Peyghambarian (1997) Design and synthesis of chromophores and polymers for electro-optic and photorefractive applications, *Nature* **388**, 845
- Chun, H., N. J. Kim, W. J. Joo, J. W. Han, C. H. Oh, and N. Kim (2002) Synthesis and characterization of organic photorefractive glass, *Synthetic Metals* **129**, 281
- Clays, K. and A. Persoons (1991) Hyper-Rayleigh scattering in solution, *Phys. Rev. Lett.* **66**, 2980
- Song, N. W., T. Kang, S. C. Jeoung, S. Jeon, B. R. Cho, and D. Kim (1996) Improved method for measuring the first-order hyperpolarizability of organic NLO materials in solution by using the hyper-Rayleigh scattering technique, *Chem. Phys. Lett.* **261**, 307
- Maker, P. D., R. W. Terhune, M. Nisenoff, and C. M. Savage (1962) Effects of Dispersion and Focusing on the Production of Optical Harmonics, *Phys. Rev. Lett.* **8**, 21
- Herman, W. N. and L. M. Hayden (1995) Maker fringes revisited: second-harmonic generation from birefringent or absorbing materials, *J. Opt. Soc. Am. B* **12**, 416
- Jung, C. and B. K. Rhee (2002) Simultaneous determination of thickness and optical constants of polymer thin film by analyzing transmittance, *Appl. Opt.* **41**, 3861
- Moylan, C. R., R. J. Twieg, V. Y. Lee, S. A. Swanson, K. M. Betterton, and R. D. Miller (1993) Nonlinear optical chromophores with large hyperpolarizabilities and enhanced thermal stabilities, *J. Am. Chem. Soc.* **115**, 12599
- Oudar, J. L. and D. S. Chemla (1977) Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment, *J. Chem. Phys.* **66**, 2664
- Song, O. K., J. N. Woodford, and C. H. Wang (1997) Effects of Two-Photon Fluorescence and Polymerization on the First Hyperpolarizability of an Azobenzene Dye, *J. Phys. Chem. A* **101**, 3222
- Singer, K. D., M. G. Kuzyk, and J. E. Sohn (1987) Second-order nonlinear-optical processes in orientationally ordered materials: relationship between molecular and macroscopic properties. *J. Opt. Soc. Am. B* **4**, 968
- Boyd, G. T., C. V. Francis, J. E. Trend, and D. A. Ender (1991) Second-harmonic generation as a probe of rotational mobility in poled polymers, *J. Opt. Soc. Am. B* **8**, 887
- Banach, M. J., M. D. Alexander, S. Caracci, and R. Q. Vaia (1999) Enhancement of Electrooptic Coefficient of Doped Films through Optimization of Chromophore Environment, *Chem. Mater.* **11**, 2554
- Dalton, L. R., W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amenda, and A. Jend

(1999) From molecules to opto-chips: organic electro-optic materials, *J. Mater. Chem.* **9**, 1905

18. Laue, T. and A. Plagens (1998) *Named Organic Reactions*, Technical University, Braunschweig, Germany, 164.S