

Second harmonic generation with DSR1 – PMMA polymer films

H Tajalli, E Mohajerani, S Ahmadi and R Kheradmand
 Center for Applied Physics and Astronomical Research, Tabriz University, Tabriz, Iran

(Received 22 January 2000; in final form 3 July 2000)

Abstract

The poling process of polymers doped with chromophores is of great importance for the nonlinear properties of these materials. So, after having optimized the poling condition the second harmonic generation (SHG) was measured for PMMA polymer doped with Disperse Red 1. The dependence of SHG intensity to the poling voltage and poling temperature have been experimentally studied. The relaxation of dopant orientation in the polymer matrix was also measured.

Keywords: NLO, Maker fringes, chromophores orientation, second harmonic generation, polymer

1. Introduction

In recent years, organic materials with second – order nonlinear optical (NLO) properties have been extensively studied for use in photonic applications such as high speed photonic switching, subpicosecond devices, electrooptic modulators, components of optical communication systems, directional couplers, parametric oscillations and other photonic devices [1, 2].

For practical applications, these NLO organic materials must retain high optical quality thin films, high optical damage thresholds, sufficiently large and stable NLO susceptibilities, low optical propagation loss and feasibility of device fabrication.

Although it is extremely difficult to synthesize materials which possess the material requirements for practical applications, numerous approaches have been developed to utilize these NLO polymeric materials for use in real applications and the performance of the organic materials has been enhanced [3-4].

However, the thermal stability of the NLO orientation alignment, optical nonlinearity and optical loss are needed to improve for device applications. Only non-centrosymmetric molecules can possess a second-order nonlinear response, i.e., they have a nonvanishing



Figure 1. π -conjugated system with acceptor and donor groups.

first molecular hyperpolarizability. Polar molecules with donor and acceptor groups connected by a conjugated π -electron systems are traditional organic second-order materials (Figure 1).

For macroscopic non-centrosymmetry, such molecules are poled in host materials using a static electric field. Corona poling [5, 6] is a powerful method for creating a large potential across the film that efficiently orients the NLO dopants non-centrosymmetrically in the polymer matrix, thereby generating large second harmonic generation SHG intensities [6-7]. Ion penetration and other surface, and spacecharge effects [6] that occur at the film surface and in the bulk during corona poling affect the magnitude and temporal stability of the SHG intensity after poling. This has a technological significance for practical processing and device applications and provides insight into the mechanics that allow these materials to be poled and the dopants to be oriented.

Two different experimental techniques have been widely used to measure NLO coefficients. The first method is concerned with the possibility of obtaining phase matching between the fundamental and the harmonic waves [8-9]. The second method of measuring NLO coefficients can be used for all material, whether phase matchable or not. It is the technique used by Maker et al. [10] on quartz to demonstrate the interference between the bound and free harmonic waves. By varying the incidence angle of a laser beam on a plane parallel sample of NLO material, the intensity of the second harmonic generated and transmitted is found to oscillate in a periodic fashion.

According to Herman and Hayden [11], the intensity of the second harmonic signal of Maker fringes when the sample has significant absorption in the frequency of the second harmonic signal is given by

$$P_{2\omega}^{\gamma \rightarrow p} = \frac{128\pi^3 |t_{af}^{1\gamma}|^4 |t_{fs}^{2p}|^2 |t_{sa}^{2p}|^2}{cAn_2^2 C_2^2} P_{\omega}^2 \left(\frac{2\pi L}{\lambda} \right)^2 d_{\text{eff}}^2 \times \exp[-2(\delta_1 + \delta_2)] \frac{\sin^2 \psi + \sin^2 \chi}{\psi^2 + \chi^2} \quad (1)$$

$$\psi = \left(\frac{2\pi L}{\lambda} \right) (n_1 C_1 - n_2 C_2),$$

$$\delta_1 = \left(\frac{2\pi L}{\lambda} \right) (n_1 \kappa_1 / C_1),$$

$$\delta_2 = \left(\frac{2\pi L}{\lambda} \right) (n_2 \kappa_2 / C_2),$$

$$\chi = \delta_1 - \delta_2 = \left(\frac{2\pi L}{\lambda} \right) \left(\frac{n_1 \kappa_1}{C_1} - \frac{n_2 \kappa_2}{C_2} \right),$$

$$t_{af}^{1\gamma} = \begin{cases} \frac{2 \cos(\theta)}{C_1 + n_1 \cos(\theta)} & , \gamma = p \\ \frac{2 \cos(\theta)}{\cos(\theta) + n_1 C_1} & , \gamma = s \end{cases}$$

$$t_{fs}^{2p} = \frac{2n_2 C_2}{n_{2s} C_2 + n_2 C_{2s}}$$

$$t_{sa}^{2p} = \frac{2n_{2s} C_{2s}}{n_{2s} \cos(\theta) + C_{2s}}$$

where $d_{\text{eff}} = -e_2 \cdot \hat{d} : \hat{e}_1 \hat{e}_1$, θ is the incident angle, P_{ω} is the intensity of the fundamental wave, λ is the wavelength of the fundamental wave, A is the area of the beam, c is the velocity of light; t_{af} , t_{fs} , t_{sa} are the transmittance coefficients of air to the nonlinear medium, to the glass plate and the glass plate to air respectively and

$$S_m = \left(\frac{1}{n_m} \right) \sin \theta, C_m = (1 - S_m^2)^{1/2}$$

The complex refractive index is $n_m = n_m (1 + ik_m)$. Subscripts 1, 2, are the fundamental wave and second harmonics respectively. When the nonlinear material has $C_{\infty v}$ symmetry, with $d_{15} = d_{31}$ from the assumption of Kleinman symmetry,

$$d_{\text{eff}} = \begin{cases} 2d_{31} C_1 S_1 C_2 + d_{31} C_1^2 S_2 + d_{33} S_1^2, & \lambda = p \\ d_{31} S_2, & \lambda = s \end{cases}$$

From simple thermodynamic consideration's it can be shown that the second harmonic coefficient component

$$d_{33}(-2\omega, \omega, \omega) = N \cdot f^{2\omega} \cdot f^{\omega} \cdot f^{\omega} \cdot \beta_{zzz} \frac{\epsilon(n_m^2 + 2) \mu E_p}{n_m^2 + 24 \cdot 5KT} \quad (2)$$

Where N is the number of NLO molecules, $f^{2\omega}$, f^{ω} are local fields factors that modify the value of the external electric field at the molecule due to contributions from neighbouring molecules, E_p : the poling field, μ : dipole moment of the NLO molecules, ϵ : the static dielectric constant, $\mu E_p / 5kT$ is a parameter connected to the competition between field induced alignment and thermal averaging of the molecules.

This competition leads us to investigate the influence of the external field, the temperature of poling process and the relaxation of NLO molecules orientation on the nonlinear optical properties.

2. Experiment

The samples were a mixture of an optically transparent polymer, poly-(methylmethacrylate) (PMMA), and a NLO dye DSR1 with 2-5 wt% dissolved into a common solvent dichloromethane (DCM).

The solution was used to form a film onto an indium tin oxide (ITO) coated glass by dip coating. Typical film thickness ranged from 2 to 6 μm .

The absorption spectrum measured in the experiment by a Spectroinc Spectrophotometer Model GENESYS 5 is shown in figure 3.

The corona discharge was generated by a tungsten needle biased with up to 6Kv placed 1.2 cm above and normal to the polymer film.

The experimental setup used for SHG measurements is shown in Figure (2). The Q-switched $\text{Nd}^{3+}/\text{YAG}$ laser was used (1.064 μm ; 10 Hz, pulse width 10ns) as the fundamental wave source. The sample cell was able to rotate owing to a stepper motor stage. The second harmonic intensity was measured by varying the incident angle of fundamental wave from -60° to 60° by the step of 0.9° .

3. Experimental results and discussion

As it is clear from Figure 3, the sample exhibits an absorption at a wavelength of the second harmonics signal and almost no absorption takes place at the fundamental wave of 1064 nm. So, according to the

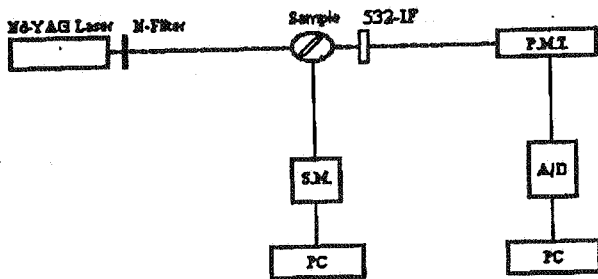


Figure 2. Experimental setup for SHG, N. filter; Neutral density filter, 532-nm interference filters, S: sample, PC: Personal Computer, S.M: stepper motor and controller, A/D: analog-to-digital converter.

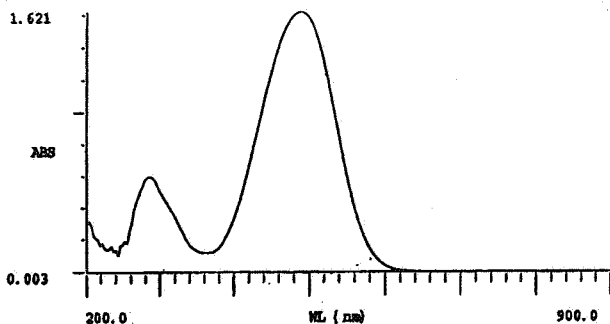


Figure 3. The absorption spectrum of PMMA-DSR1 film.

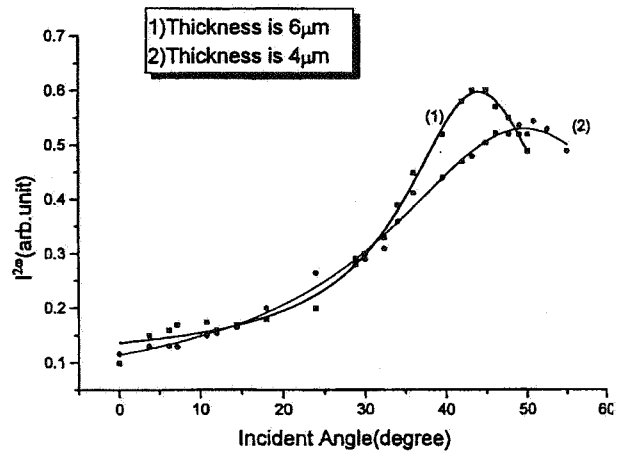


Figure 4. Maker fringe pattern, angular distribution of the SH intensity of organic film at thickness of 6 μm , poling voltage of 5Kv and poling temperature of 80° .

theoretical study of Herman and Hayden and the experimental emphasis of Tong Kun Lim et al. the intensity of the second harmonic generation in our samples should follow equation (1) [11, 12].

Figure 4 shows the angular distribution of the second harmonic intensity of the organic film of 6 μm thickness. In this sample no fringes were observed but there was just an increase of the SH with increasing angle of incidence. This is because the range of accessible optical path lengths in the sample is smaller than one coherence length. At higher angles, the higher SH intensity occurs due to the phase mismatch of the bound nonlinear polarization wave and the free propagating second harmonic radiation field.

The effect of poling temperature on the second harmonic intensity has also been studied for PMMA doped with 2-5% dye in weight. Figure 5 shows the plot of $I^{2\omega}$ versus poling temperature which exhibits a maximum around 80 degrees. This temperature is slightly below the glass transition temperature of the guest-host system, which is around 100 degrees due to the dye plasticizing effect. On the one hand, at low temperatures, a high viscosity of the medium prevents the NLO molecules from moving easily. On the other hand at higher temperatures the thermal randoming effect disturbs the molecules orientation. 80 degrees seems a good compromise between these two effects.

The poling voltage was always applied at temperatures around glass transition temperature, resulting in a build up of the SH signal owing to the imposed molecular orientation process. To study the

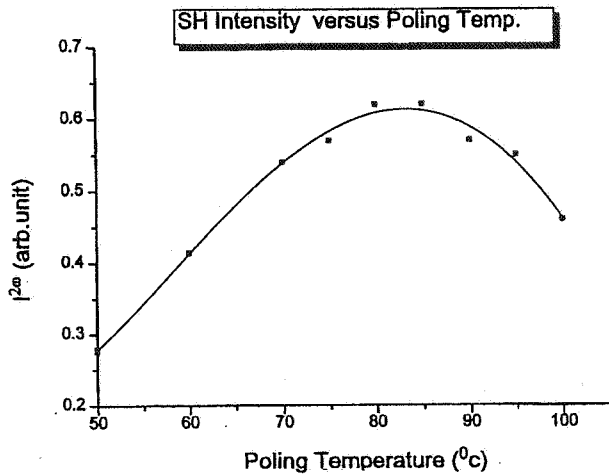


Figure 5. Intensity of SH wave for various poling temperatures at a incident angle of 45° and poling voltage 5Kv.

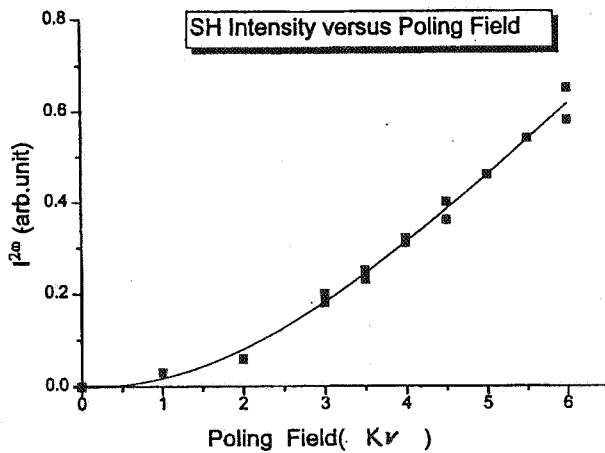


Figure 6. The second harmonic intensity versus poling field.

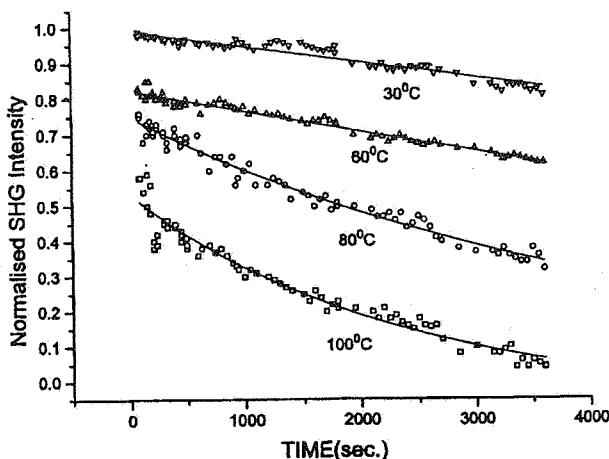


Figure 7. Decay of SHG signal for a set of DSR1-PMMA samples at different temperatures.

dynamics of the rise of the induced noncentrosymmetry, the influence of the poling field on second harmonic

coefficient was investigated. Figure 6 shows the SH intensity versus poling field which increases according to the square of the poling field (E_p). These results are in a good agreement with the relation (2) introduced by Singer et al.

The relaxation of dopant orientation in the polymer matrix after poling can be observed by monitoring SHG intensity. Figure 7 shows the experimental data for normalized SHG intensity at different temperatures for a set of similar samples of PMMA-DSR1 films. The diagrams show that the second order NLO properties of the samples reduced as the orientational order of the medium is lost, and this reduction is faster for higher temperatures.

This relaxation behaviour of DSR1 chromophores orientation in PMMA-DSR1 films is in a good agreement with the model based on the stretched exponential functions $\psi(t) = \exp(-t/\tau)$, $\tau = 4\pi\eta R/KT$ where η , T , R and μ are viscosity, temperature, radius of dipolar and dipole moment respectively.

4. Conclusion

The second harmonic generation was observed in PMMA polymer doped with DSR1. It was shown that the orientational order in polymer film is governed by the distribution function and is inversely proportional to the temperature. Increasing the temperature increases the mobility of the chromophores. The experimental results show that the optimum poling temperature is around the glass transition temperature of the doped polymer film.

It was shown that the increase in the applied poling voltage increases the SHG intensity. However, at sufficiently high fields, dielectric breakdown takes place which reduces the poling efficiency. A quadratic relation between the poling voltage and the SHG intensity at the polymer film was observed.

The relaxation of dopant orientation in the polymer matrix was measured by monitoring SHG intensity after poling. It was seen that the second order NLO properties of the samples reduced as the orientational order of the medium was lost, and this reduction was faster for higher temperatures.

Reference

1. H J Lee, S J Kang, H N Cho, J T Park, and S K Choi, *Macromolecules*, **28**, 4638 (1995).

2. D R Robello, P T Dao, J S Schildkout, M Scozzafava, E J Urankar and C S Willan, *Chem. Mater.* **7**, 284 (1995).
3. D M Burland, R D Mrlle, and C A Walsh, *Chem. Rev.* **94**, 31 (1994).
4. G A Lindsay and K D Singer, Polymers for second-order nonlinear optics, ACS symp, ser. Vol. 601, *American chemical society*, Washington DC (1995).
5. H L Hapsch, J Yang, G K Wong, and J M Torkelson, *Macromolecules.* **21**, 526 (1988).
6. H L Hampsch, G K Wong, J M Torkelson, *Polym. Commun.* **30**, 40 (1989).
7. K D Singer, J E Sohn, and S J Lalama, *Appl. Phys. Lett.* **49**, 248 (1986), K D Singer, M G Kuzyk, and J E Shohn, *J. Opt. Soc. Am.* **B4**, 968 (1987).
8. G E Francois, *Phys. Rev.* **143**, 597 (1966).
9. J E Bjorhhoim and A E Siegman, *Phys. Rev.* **154**, 851 (1967).
10. P D Maker, R W Terhune, M Nisunoff, and C M Savage, *Phys. Rev. Lett.* **8**, 21 (1962).
11. W N Herman and L Michael Hayden, *J. Opt. Soc. Am.* **B12**, 416-427 (1995).
12. T K Lim, M Y Jeong, C Song and D C Kim, *Applied Optics*, **37**, 13 (1998).