

# **EFISHG studies of chromophore orientational dynamics in photorefractive polymers**

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## **Abstract**

Photorefractive (PR) polymers are promising candidates for various applications that require fast response times. The main factors that determine the PR speed in polymers are photoconductivity and chromophore reorientation in an electric field. In this paper, we investigate the chromophore reorientational dynamics in various PR composites using the electric field second harmonic generation (EFISHG) technique, and then relate it to the PR dynamics as observed in a four-wave mixing (FWM) holographic experiment. We also report on the enhancement of the EFISHG signal in the presence of HeNe light, which we attribute to a photoinduced internal electric field formed in the PR polymer.

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## I. INTRODUCTION

Photorefractive (PR) polymers are potentially useful for dynamic applications such as optical data processing. This has resulted in several studies aimed at determining the factors that limit the PR grating formation speed [1–4]. The dynamics of the PR effect are determined by (i) the generation of the non-uniform space-charge field and (ii) the chromophore orientational dynamics in the presence of the evolving space charge field. The chromophore orientational dynamics in the electric field is the subject of this paper while the space charge dynamics is reported elsewhere[1].

The most common experimental methods used for probing chromophore orientational mobility in poled polymers are nonlinear optical (NLO) techniques [5–7] and ellipsometric techniques [8, 9]. Ellipsometric (ELP) techniques involve a measurement of the changes of the refractive index owing to the induced birefringence and the electro-optic effect [8, 9]. The drawback of the ELP techniques is its low sensitivity compared to the NLO techniques, which limits its application. Nonlinear optical techniques provide much better signal-to-noise ratios than ellipsometric techniques. Thus, we have chosen an NLO technique, electric field induced second harmonic generation (EFISHG), for these molecular orientation studies. In this paper, we measure the speed of chromophore reorientation in the electric field in various PR polymer composites previously studied [1, 10] and relate the orientational speed measured by EFISHG to the speed of PR grating formation. We will comment on the conditions under which the orientational speed limits the PR grating formation speed. In a later section, we also describe a light-induced enhancement of the EFISH signal.

## II. EFISHG AS A PROBE OF CHROMOPHORE REORIENTATION

### A. Theory

One of the requirements for a PR material [11] is that the material must exhibit a linear electro-optic effect requiring that the material lack an inversion center [12]. Photorefractive polymer composites are naturally isotropic as produced. Thus, for the electro-optic effect to exist, the centrosymmetry of the material needs to be broken. This can be achieved with an applied electric field, either in a pre-poling step for high (relative to room temperature) glass transition temperature ( $T_g$ ) composites or *in situ* for low- $T_g$  composites. In an external

electric field, the dipolar NLO chromophores align in the direction of the applied field. This alignment changes the symmetry of the composite to  $C_{\infty v}$ , which then lacks inversion symmetry and, therefore, admits the electro-optic effect. Also, the orientational enhancement effect due to the high orientation mobility of the chromophores in low- $T_g$  PR polymers [13] *in situ* is one of the main mechanisms leading to the refractive index change in the PR effect. Therefore, the chromophore alignment in both the external and space charge fields is an important feature of the PR polymer composites.

EFISHG is a well-established technique to determine the second order nonlinear optical response of molecules [14], although the third order nonlinearity contributes as well. Generally, EFISHG can be viewed as a third order process that can be described by the nonlinear polarization

$$P_i^{2\omega} = \chi_{ijkl}^{(3)}(-2\omega; \omega, \omega, 0) E_j^\omega E_k^\omega E_l^0 \quad (1)$$

where  $E_{j,k}$  are the optical fields, and  $E_l^0$  is the applied electric field.

When an electric field is applied to isotropic polymers doped with NLO chromophores, the dipole moments of the chromophores couple to the electric field causing a partial orientation of the dipolar molecules. This can be viewed as breaking the symmetry of the material allowing bulk coherent second harmonic generation. Consequently, Eq. 1 can be rewritten in a form that resembles the second order nonlinear effect

$$P_i^{2\omega} = \chi_{ijk}^{(2)}(-2\omega; \omega, \omega)(E^0) E_j^\omega E_k^\omega \quad (2)$$

where the applied electric field dependent second order susceptibility

$$\chi_{ijk}^{(2)}(-2\omega; \omega, \omega)(E^0) = \chi_{ijkl}^{(3)}(-2\omega; \omega, \omega, 0) E_l^0$$

has been introduced.

In a low electric field limit of the thermodynamic model [14], for the simplest case of the optical fields parallel to the applied field, the electric field dependent susceptibility  $\chi_{zzz}^{(2)}(E_0)$  of Eq. 2 is given by [14]:

$$\chi_{zzz}^{(2)}(E_0) = N f^0 f^2(\omega) f(2\omega) \left( \gamma + \frac{\beta m^*}{5kT} \right) E_0 \quad (3)$$

where

$$\gamma = \frac{1}{15} \sum_{u,v=x,y,z} (2\gamma_{uuvv} + \gamma_{uvvu})$$

and

$$\beta m^* = \frac{1}{3} \sum_{u,v=x,y,z} (2\beta_{uvv} m_v^* + \beta_{uvv} m_u^*).$$

Here  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are the first and second hyperpolarizabilities respectively, and  $m^*$  is the dressed molecular dipole moment [14]. In our experimental geometry to be described in the next section, it is not only  $\chi_{zzz}^{(2)}(E_0)$  but rather a mixture of different components of the  $\chi^{(2)}(E_0)$ -tensor that contributes, and the measured quantity is the intensity of second harmonic light  $I(2\omega) \sim P^2(2\omega) \sim (\chi^{(2)})^2$  that combines all the components. However, since we are interested in the transient characteristics, the magnitude of the measured intensity need not be scaled.

The most relevant component  $\chi_{zzz}$  of Eq. 3 as well as the other components of the  $\chi$ -tensor, contain two separate contributions - from the second order polarizability  $\beta$  and the third order polarizability  $\gamma$ . The third order ( $\gamma$ ) electronic contribution appears instantaneously when the electric field is applied, even in centrosymmetric materials, while the second order ( $\beta$ ) contribution arises as the chromophores become aligned and is the feature of non-centrosymmetric materials of interest here.

We need not go into detail in elucidating the combinations of the  $\chi^{(2)}$ -tensor components that contribute to the second harmonic signal in our experimental geometry. It is sufficient for measuring dynamics to assume that the second harmonic response of the material to the applied electric field, measured with EFISHG technique, is derived from Eq. 3

$$I(2\omega) \sim \left( \gamma + \frac{\beta m^*}{5kT} \right)^2 E_0^2 \quad (4)$$

As mentioned above, the time evolution of the second harmonic signal  $I(2\omega)(t)$  can be considered as a two-step process: first, the instantaneous signal due to the  $\gamma$ -part appears; then the slow signal due to chromophore orientation (the  $\beta$ -part) evolves. In practice, the  $\gamma$ -part of the signal is at least an order of magnitude smaller than the orientational part [14].

## B. Experiment

The PR polymer composites used in our study were described elsewhere [1] and consisted of PVK as the photoconductor, C<sub>60</sub> as the sensitizer, BBP as the plasticizer and 5CB, PDCST, and AODCST as the nonlinear chromophores (NLO) [1, 10]. We studied both

unplasticized (high  $T_g \sim 150^\circ$ ) composites PVK(99-x%)/C<sub>60</sub>(1%)/NLO(x%), where x varied from 1-20 %, and plasticized (low  $T_g \sim 20^\circ$ ) composites PVK(49%)/C<sub>60</sub>(1%)/BBP(50-y%)/NLO(y%), where y varied from 1-40%. Sample preparation consisted of the following steps. First, PVK was dissolved in a mixture of toluene and cyclohexanone wt. 4:1. Then, C<sub>60</sub> was dissolved in toluene and added to a solution of PVK. Finally, the dye was added to a solution of PVK and C<sub>60</sub>. Then, we prepared the films on ITO slides, sandwiched them together and baked them in a vacuum oven for 1h. The thickness of the samples varied from 30-70 $\mu$ m.

We used a mode-locked Ti:Sapphire laser pumped with an  $Ar^+$  laser. At a pump power of 6 mW, the average output power of the Ti:Sapphire laser was  $\sim 0.5$  mW. The pulse duration was  $\sim 50$  fs, and the wavelength range  $\sim 760-800$  nm. The light of fundamental frequency  $\omega$  was obliquely incident on the sample, and the second harmonic ( $2\omega$ ) signal generated in the sample upon application of the electric field was detected with a photomultiplier tube (PMT). To minimize low-frequency noise, we implemented lock-in detection using the fundamental light modulated with a chopper. For polarization measurements, a polarization rotator before the sample and a polarizer between the sample and the PMT were used. A filter that blocked the fundamental frequency  $\omega$  and transmitted the second harmonic signal light of  $2\omega$  was placed after the sample.

The experimental run was as follows. First, with no applied electric field, the noise level was recorded. Then, the electric field was turned on, and the rise of the second harmonic signal was monitored. When the signal reached a steady-state, the electric field was switched off, and the second harmonic decay observed. The switching time of the power supply was below 5 ms. This is at least an order of magnitude faster than the orientation times obtained from the EFISHG transients in our composites. Thus, we ensured that our measurements are not the artifacts due to equipment, but are indeed related to the chromophore orientation. The experiment was performed at electric fields typically from 5–60 V/ $\mu$ m.

According to symmetry considerations, our system, which under applied electric field, is expected to possess the  $C_{\infty v}$  symmetry, should exhibit only p-polarized second harmonic light [15]. In other words, from four possible combinations of the incident and second harmonic (SH) light linear polarizations ( $p$ -fundamental,  $p$ -SH;  $p$ -fundamental,  $s$ -SH;  $s$ -fundamental,  $p$ -SH, and  $s$ -fundamental,  $s$ -SH), only  $pp$  and  $sp$  configurations produce the SH signal in a material with  $C_{\infty v}$  symmetry. In polarization dependent measurements, only  $pp$  and  $sp$

signals were observed, confirming that the symmetry of the composites is indeed as expected.

### III. RELATIONSHIP BETWEEN THE ORIENTATIONAL TIMES MEASURED IN EFISHG AND FWM

In this section the orientational response as measured in the EFISHG experiment is related to the photorefractive grating dynamics due to orientational processes.

For this, we consider the chromophore orientation as the reorientation of a rigid dipolar molecule in an isotropic medium described by Debye rotational diffusion [16, 17]. In this model, the dynamics of the orientational distribution function  $f(\theta, t)$  is given by the classical rotational diffusion equation:

$$\frac{1}{D} \frac{\partial f(\theta, t)}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left\{ \sin \theta \left[ \frac{\partial}{\partial \theta} f(\theta, t) + \frac{1}{kT} \frac{\partial U}{\partial \theta} f(\theta, t) \right] \right\} \quad (5)$$

where  $D$  is the rotational diffusion constant.  $U$  is the interaction energy between the electric field  $E_0$  and the dipolar molecule given by  $U = mE_0 \cos \theta$ , where  $m$  is the molecular dipole moment.

The orientational dynamics as measured by various techniques can be expressed through the  $n^{\text{th}}$  order moments  $\langle \cos^n \theta(t) \rangle$  of the orientational autocorrelation functions (OACF)  $\Phi_n(t)$  [16]. For example, in the low electric field limit ( $mE_0 \ll kT$ ), the susceptibility  $\chi^{(2)}(E_0)$  determined in the EFISHG experiment is proportional to the first moment:

$$\chi^{(2)}(E_0) \sim \Phi_1(t) \sim \langle \cos \theta(t) \rangle,$$

and the birefringence  $\Delta n(t)$  is proportional to the second moment:

$$\Delta n(t) \sim \Phi_2(t) \sim \langle \cos^2 \theta(t) \rangle.$$

Therefore, the time evolution of the EFISHG signal is determined by the dynamics of the first moment

$$I(2\omega)(t) \sim (\chi^{(2)}(E_0))^2 \sim \Phi_1^2(t).$$

The rise transient of the first moment is given by

$$\Phi_1(t) \sim (1 - \exp[-D_1 t]),$$

where  $D_n = n(n+1)D$  and thus,  $D_1 = 2D$ . Therefore, the rise of  $\sqrt{I(2\omega)(t)}$  is described by the speed  $D_1 = 2D$ .

The temporal development of the orientationally enhanced diffraction efficiency  $\eta$ , as measured in the four-wave mixing (FWM) experiment, can be expressed in terms of the constants  $D_n$  [9]:

$$\eta \sim \{A_1[1 - \exp(-D_1t)] + A_2[1 - \exp(-D_2t)]\}^2$$

Then, the orientational dynamics of the  $\sqrt{\eta}$  is also given by two inverse time constants -  $D_1 = 2D$  and  $D_2 = 6D$ .

Summarizing the rotational diffusion approach, from the EFISHG experiment, the constant  $D_1$  can be determined and compared to the slower inverse time constant of the diffraction efficiency. The faster component  $D_2$  can be calculated from the theory assuming that the relation  $D_2 = 3D_1$  is valid.

The diffraction efficiency dynamics depends on both photoconductivity and orientational speed. Thus, the orientational contribution is not easily isolated. The diffraction efficiency rise is often fit to a bi-exponential function, in which one component of the PR speed is determined by the photoconductivity, and another one by the orientation. In this case, the two inverse time constants -  $D_1$  and  $D_2 = 3D_1$  are approximated by a single time constant in the biexponential fit. Another issue that must be kept in mind is that the orientational speed as observed in both EFISHG and FWM, is electric field dependent. The only electric field in the EFISHG experiment is the applied field. In contrast, in the FWM experiment, both the electric fields due to the projection of applied field on the grating vector and the space charge field act on the chromophores. Since EFISH is measured with only an externally applied field, one must keep in mind that the effective field for the FWM measurement will also have a space charge component, which also contributes. However, we found the field dependence of the speed weak enough that our measurements should provide a reasonable estimate of the diffusion constants. Also, both thermodynamic models used to derive Eq. 4 and rotational diffusion model (Eq. 5) assume the system of freely rotating dipoles corresponding to the polymer composite at temperatures above  $T_g$  which is the case for our plasticized composites and not the case for unplasticized ones. Nevertheless, we proceed and believe that reasonable estimates can be made, and the relationship between EFISHG and FWM orientational dynamics established. In any case, we can distinguish the time scales where the orientational dynamics will contribute to the observed PR dynamics.

As an example of relating the orientational dynamics observed in EFISHG and FWM experiments, we consider the composites **(1)** PVK(79%)/ $C_{60}$ (1%)/5CB(20%) and **(2)**

PVK(49%)/C<sub>60</sub>(1%)/BBP(45%)/AODCST(5%) (Figures 1 and 2). The EFISHG measurements were performed at the electric field  $E_a$  equal to the projection of applied electric field on the grating vector  $\tilde{E}_a$  in the FWM measurements. Composite **(1)** is a relatively high  $T_g$  composite ( $T_g \sim 80^0 C$ ), so that at room temperature the chromophore orientation is expected to be slower than for the composite **(2)** which has  $T_g \sim 20^0 C$ . This is supported by the experimental data: the single exponential fits of the  $\sqrt{I(2\omega)(t)}$  shown in Figures 1 and 2 yield the coefficients  $D_1 = 0.48 \pm 0.02 s^{-1}$  and  $D_1 = 19.6 \pm 2.6 s^{-1}$  for these two composites respectively.

Let us now analyze the diffracted signal as measured in the FWM experiment. For both composites, we fit the transients  $\sqrt{\eta(t)}$  to a bi-exponential  $\sqrt{\eta(t)} \sim (1 - a \exp[-\nu_1 t] - (1 - a) \exp[-\nu_2 t])$ . For the transient shown in Figure 1 (composite PVK(79%)/C<sub>60</sub>(1%)-/5CB(20%)), the fit yields  $\nu_1 = 6.1 \pm 0.5 s^{-1}$  and  $\nu_2 = 1.1 \pm 0.2 s^{-1}$ . Comparing these constants to the orientational constant  $D_1$  for this composite, we conclude that while the faster component  $\nu_1$  is much larger than the orientational speed  $D_1 = 0.48 s^{-1}$ , the slower component  $\nu_2$  is rather close. Indeed, the faster component  $\nu_1$  is found to be intensity dependent and is attributed to photoconductivity [1]. The slower component  $\nu_2$  is intensity independent and can be attributed to the chromophore orientation. As we discussed above, the average orientational speed as measured in the FWM experiment can yield values ranging from  $D_1$  to  $D_2 = 3D_1$ . The constant  $\nu_2 = 1.1 s^{-1}$  fits in the range of  $0.48 - 1.44 s^{-1}$ , which confirms it is attributable to orientational.

For the transient shown in Figure 2 (composite **(2)**), the  $\sqrt{\eta(t)}$  bi-exponential fit yields  $\nu_1 = 0.52 \pm 0.02 s^{-1}$  and  $\nu_2 = 0.049 \pm 0.001$ . If one compares these constants to the orientational speed  $D_1$  determined from EFISHG, one concludes that since the orientational speed is much higher than both the  $\nu_1$  and  $\nu_2$  photorefractive speed components, neither can be attributed to orientation. Indeed, as our FWM experiments showed, both  $\nu_1$  and  $\nu_2$  are intensity dependent and determined by the photoconductivity [1].

#### IV. EFISHG STUDY OF INTERNAL ELECTRIC FIELDS

While performing the measurements above, we found an interesting phenomenon due to internal electric fields on which we now report. As considered in Section II A, the intensity of the second harmonic signal measured in EFISHG experiments is quadratic in electric

field (Eq. 4). Therefore, this experiment is quite sensitive to electric field changes. This property allows one to probe the space charge fields formed in the material using the EFISHG technique.

Kim *et al.* used second harmonic generation for a space-charge field measurement in the photorefractive (PR) crystal  $\text{LiNbO}_3$  doped with MgO [18]. To our knowledge, similar studies in photorefractive polymers have not been reported in the literature. As mentioned previously, the photorefractive grating formation involves different processes that occur in the material under the influence of the interfering optical beams. Since originally we set up the EFISHG experiment to probe the chromophore reorientation in the PR polymer composites, it was reasonable to check whether the presence of light other than the Ti:Sapphire laser beam used for the EFISHG measurements (see Section II B) affects the orientational processes. In particular, we were interested in how the HeNe light of  $\lambda = 633 \text{ nm}$  used for our PR measurements influences the chromophore orientational speed as measured by the EFISHG. Accordingly, we illuminated our sample with a He-Ne laser beam whose cross section is much larger than the Ti:Sapphire laser to insure a uniform optical field. The measurement we performed included the following. First, with the HeNe light blocked, we applied an electric field and monitored the rise of the second harmonic (SH) signal due to the chromophores aligning in the electric field. Then, the electric field was turned off, and the SH signal decay was observed. Second, the HeNe light was allowed through, and the experiment was repeated in the presence of the HeNe light.

We expected to see an effect on the orientational dynamics due to local field effects caused by the photoinduced space charge. We did not find a substantial difference in the dynamics. However, we did find that the second harmonic signal was enhanced in the presence of HeNe light as shown in Figure 3. We investigated several possible explanations:

*The chromophore alignment changes due to optical poling.* Since the intensity of the second harmonic is proportional to the square of the first moment of the OACF  $I(2\omega) \sim (\langle \cos \theta \rangle)^2$ . Optical poling would increase this moment leading to a higher degree of polar order and consequently a larger signal. It would also introduce a second moment due to axial alignment of the chromophores perpendicular to the polarization direction of the He-Ne light. This would appear as a change in the ratio between the **pp** and **sp** components. This was not observed.

*The effective hyperpolarizabilities  $\beta$ ,  $\gamma$  changed due to the change in local field in the*

*presence of HeNe light.* In the previous section we established the connection between the intensity  $I(2\omega)$  measured in EFISHG and the hyperpolarizabilities  $\beta$  and  $\gamma$  (Eq. 4). If the hyperpolarizabilities changed, we would be able to detect the changes in linear absorption in the presence of electric field. No changes in absorption were observed, ruling out this possibility.

*The electric field changes.* We considered that the chromophores align in the applied field  $E_0$ . However, PR polymer composites are prone to a parasitic space-charge field due to uncompensated trap filling with injected charge and non-neutralized ionic build-up at the electrodes, which screen the external electric field [1, 19]. Then, the effective poling field  $E_{pole}$  inside the sample is lower than the external field  $E_0$ . When the HeNe light is incident, free holes are generated, which then neutralize some of the surface and bulk trapped charge, and consequently increasing the internal electric field. In addition,  $C_{60}^-$  anions that are created in the photogeneration process [1, 20] may partially compensate the trapped charge, and also increase the internal electric field. Consequently, the screening field is reduced, and the intensity of the second harmonic ( $I(2\omega) \sim E_{pole}^2$ ) increases.

Evidence for this last model is now provided. First, we established that this enhancement effect in the presence of HeNe light is a result of charge photogeneration and transport from the observation that the composites without a sensitizer ( $C_{60}$ ) did not exhibit the enhancement. Also, the effect was not observed in the composites in which the photoconductor poly(N-vinyl-carbazole) (PVK) was replaced with a non-photoconductor poly(methyl-methacrylate) (PMMA). In addition, the enhancement increased as a function of HeNe light intensity (Inset in Figure 3), applied electric field and temperature, which corresponds to the trends observed in the photoconductivity.

Second, the largest enhancement was obtained in samples with high plasticizer or chromophore content. Upon application of the electric field, such composites exhibit high dark current due to ionic impurities moving towards the electrodes and uncompensated trap filling with injected charge. This is illustrated in Figure 4, which shows typical poling current dynamics for composite **(2)**. Therefore, in such composites, the screening of the applied field is larger than in unplasticized composites, so that the effect due to HeNe light is observed more readily.

Third, the initial SHG peak which appears as the electric field is applied as shown for the highly plasticized (room  $T_g$ ) composite **(2)** in Figure 3 illustrates the screening of the

external electric field. At time  $t = 65$  s, the electric field is applied, and the chromophores orient with the inverse time constant (orientational speed)  $D_1 \sim 20$  s<sup>-1</sup>. In the meantime, the impurity ions start to move towards the opposite electrodes and build-up, creating the internal field that reduces the total electric field in the sample. This reduction is accompanied by the reduction in the second harmonic signal observed (the peak in Figure 3. At  $t = 90$  s, the HeNe light is turned on, partially compensating the charge that screens the applied electric field, as we discussed above. The HeNe light is turned off at  $t = 103$  s, the screening again becomes uncompensated, and the second harmonic intensity reduces. The electric field is turned off ( $t = 108$  s) and then turned on again ( $t = 110$  s), and the peak that appeared in the beginning ( $t = 65$  s) does not appear which indicates that the internal electric field has reached equilibrium.

## V. CONCLUSIONS

We studied chromophore orientation in polymer composites under an applied electric field using the EFISHG technique. We demonstrated that the chromophore reorientation in the low- $T_g$  composite is faster than in the high- $T_g$  composite as reflected in the second harmonic generation rise when the electric field is applied. The deduced diffusion constant for the low- $T_g$  composite indicates that the orientational speed is faster than the development of space charge, and thus the orientational dynamics do not limit the PR speed. The biexponential behavior in the FWM experiment are due to the effects of two different traps in the development of the space charge field[1]. For the high- $T_g$  composite, the orientational dynamics occur on the same time scale as the development of the space charge field and, consequently, contribute to the overall PR dynamics. The relationship between orientational speed as measured in the FWM holographic experiment and EFISHG experiment was established.

A simple theoretical relationship between the orientational dynamics as observed in various experiments was established within the limitations and applicability of an oriented gas model, especially as applied to high- $T_g$  composites well below the  $T_g$ . Despite these and other limitations listed above, the technique described here helps to establish the contribution of orientational dynamics to the PR dynamics in various composites.

Also, as we showed, the sensitivity of the EFISHG technique allows one to study various processes in the chromophore-doped polymers, such as internal electric field formation inside

the material, and thus, can be used as an effective probe of internal electric fields.

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**Figure 1.** Example of data analysis for orientational dynamics studies for the high- $T_g$  composite **(1)** at  $E_a = 10V/\mu m$  (a) EFISH signal (b) FWM dynamics.

**Figure 2.** Example of data analysis for orientational dynamics studies for the low- $T_g$  composite **(2)** at  $E_a = 10V/\mu m$  (a) EFISH signal (b) FWM dynamics.

**Figure 3.** Influence of HeNe light of  $20 \text{ mW/cm}^2$  intensity on the second harmonic signal in the composite **(2)** at  $E_0 = 15 V/\mu m$ . Inset shows the relative increase of the EFISHG enhancement ( $\delta$ ) as a function of HeNe light intensity as observed in composite **(2)** at  $E_0 = 10 V/\mu m$ .

**Figure 4.** Poling current in composite **(2)** at  $E_0 = 15 V/\mu m$ . The presence of HeNe light of intensity  $10\text{mW/cm}^2$  results in a photocurrent which adds to the poling current.

Figure 1. Ostroverkhova, Stickrath, Singer

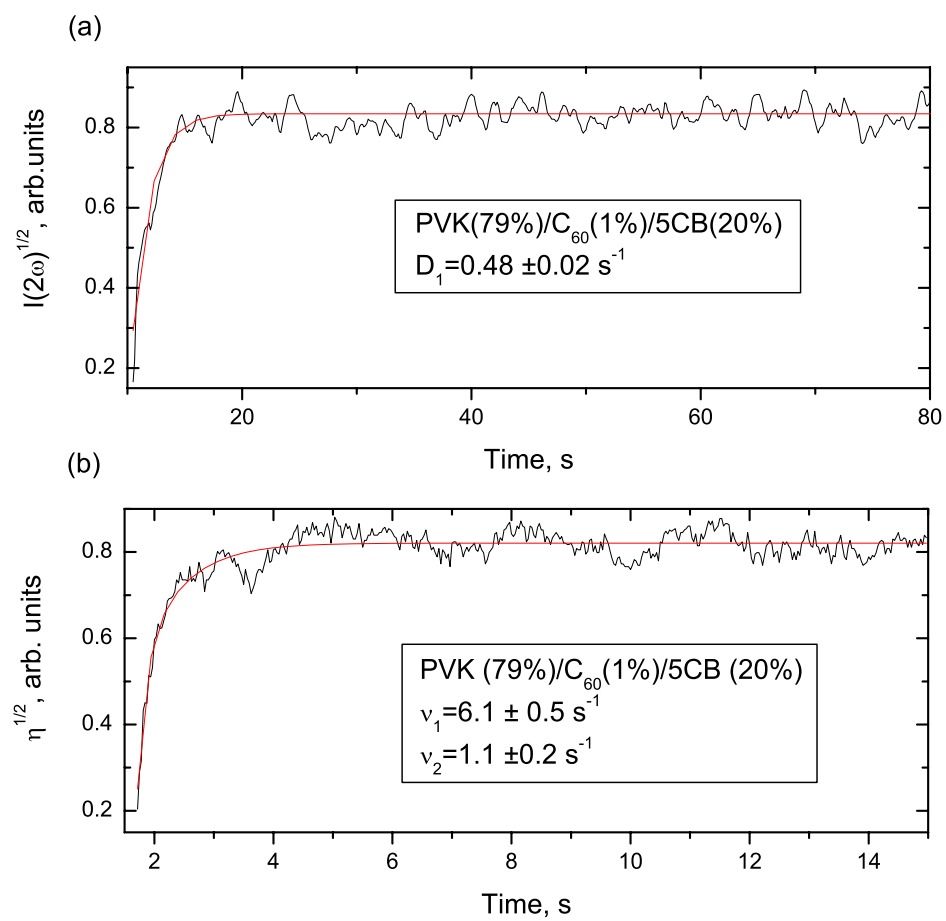


Figure 2. Ostroverkhova, Stickrath, Singer

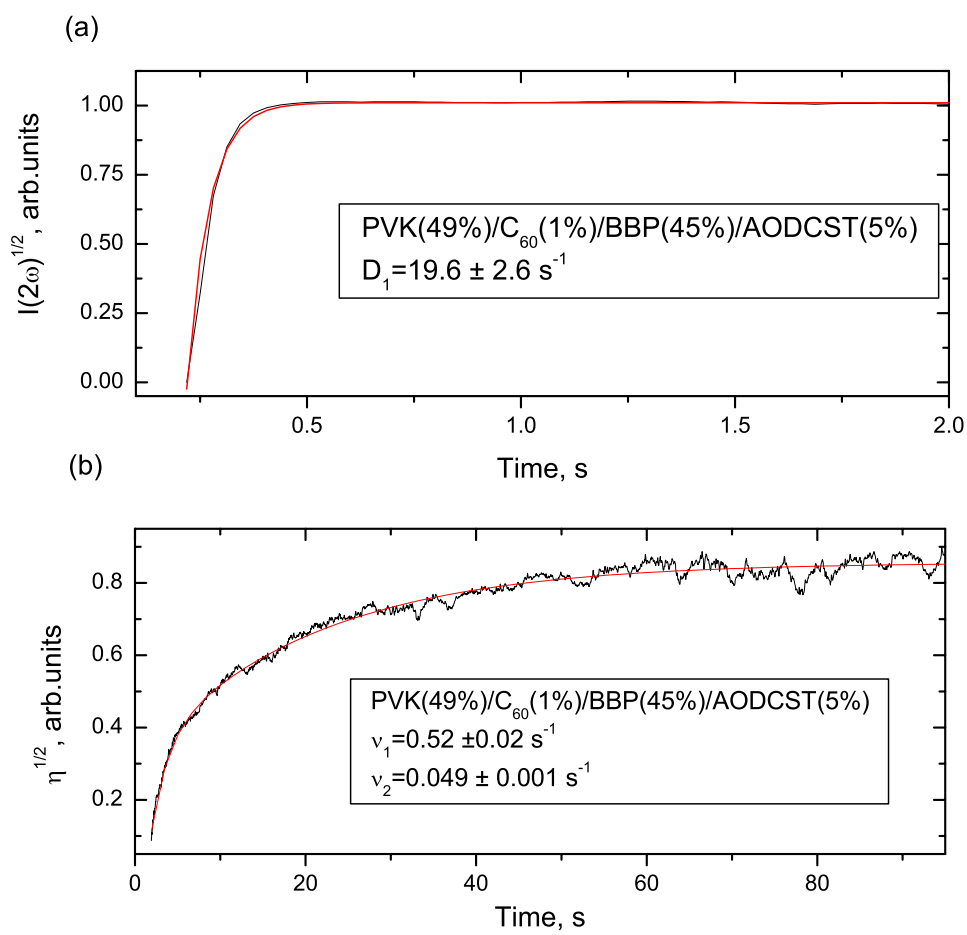


Figure 3. Ostroverkhova, Stickrath, Singer

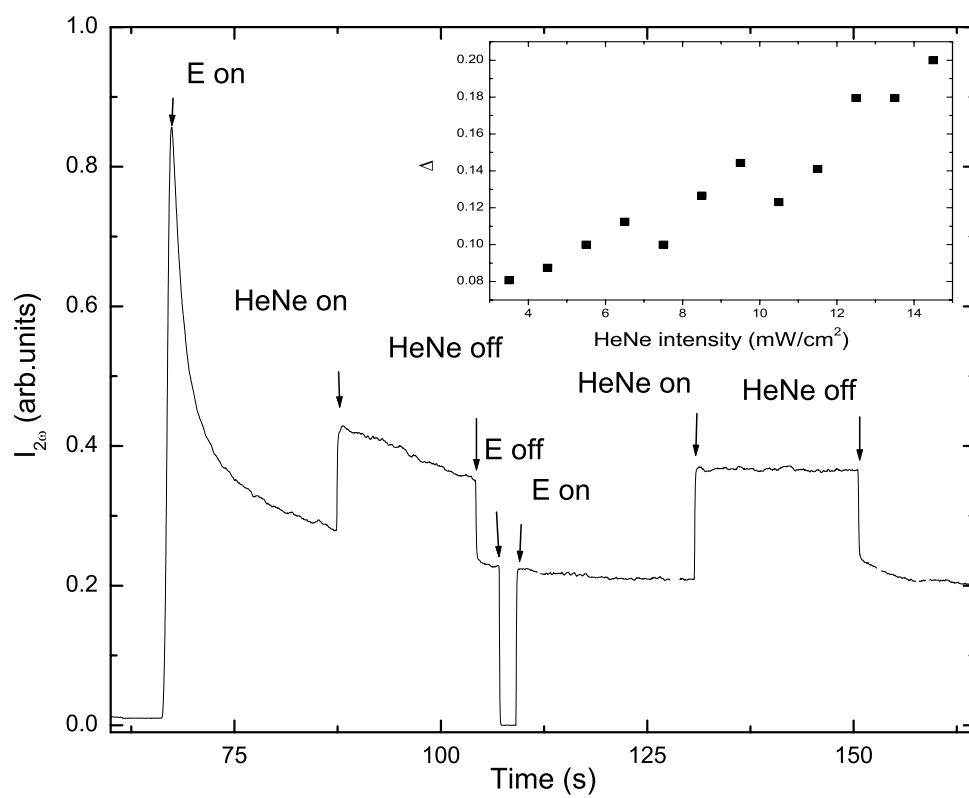


Figure 4. Ostroverkhova, Stickrath, Singer

