

Electric field-induced second harmonic generation studies of chromophore orientational dynamics in photorefractive polymers

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Photorefractive (PR) polymers are promising for use in 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 article, 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 observed in a four-wave mixing 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 that formed in the PR polymer. © 2002 American Institute of Physics. [DOI: 10.1063/1.1476974]

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 speed of PR grating formation.^{1–4} The dynamics of the PR effect are determined by (i) generation of the nonuniform space–charge field and (ii) chromophore orientational dynamics in the presence of the evolving space–charge field. The chromophore orientational dynamics in an electric field are the subject of this article and the space–charge dynamics are 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.^{8–11} Ellipsometric (ELP) techniques involve measurement of the changes in refractive index that are due to induced birefringence and the electro-optic effect.^{8,9} Another technique that is sensitive to chromophore orientation is electric field-induced second harmonic generation (EFISHG). In this article, we explore the use of this technique, which is very sensitive to the removal of the inversion center induced by action of an external electric field on the chromophore dipole moment. This sensitivity is especially useful in the dilute composites that we study here. In this article, we measure the speed of chromophore reorientation in the electric field in various PR polymer composites previously studied^{1,12} and relate the orientational speed measured by EFISHG to the speed of formation of PR grating. We will comment on the conditions under which the orientational speed limits the speed of PR grating formation. In a later section, we also describe light-induced enhancement of the EFISH signal.

II. EFISHG AS A PROBE OF CHROMOPHORE REORIENTATION

A. Theory

One requirement for a PR material¹³ is that the material must exhibit a linear electro-optic effect, that is, that the material lacks an inversion center.¹⁴ 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 applying an electric field, either in a prepoling 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, allows the electro-optic effect. Also, the orientational enhancement due to the high orientation mobility of the chromophores in low- T_g PR polymers¹⁵ *in situ* is one of the main mechanisms that leads to a change in refractive index in the PR effect. Therefore, the chromophore alignment in both the external and space–charge fields is an important feature of PR polymer composites.

EFISHG is a well-established technique with which to determine the second order nonlinear optical response of molecules,¹⁶ although third order nonlinearity contributes as well. Generally, EFISHG can be viewed as a third order process that can be described by 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 electric field applied.

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

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

in which 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,¹⁶ 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 by¹⁶

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

where

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

and

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

Here β_{ijk} and γ_{ijkl} are the first and second hyperpolarizabilities respectively, and m^* is the dressed molecular dipole moment.¹⁶ In the geometry used for our experiments, described in Sec. II B, 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 quantity measured 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 intensity measured need not be scaled.

The most relevant component, χ_{zzz} , of Eq. (3), as well as other components of the χ tensor, contain two separate contributions, one from second order polarizability β and the other from third order polarizability γ . The third order (γ) electronic contribution appears instantaneously when the electric field is applied, even in centrosymmetric materials, while the second order (β) contribution arises as the chromophores become aligned and is the feature of the noncentrosymmetric 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 electric field applied, measured with the 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 to be a two-step process: first, the instantaneous signal due to the γ part appears; then the slow signal due to chromophore orientation (the β part) evolves. In practice, the γ part of the signal is at least an order of magnitude smaller than the orientational part.¹⁶

B. Experiment

The PR polymer composites used in our study are described elsewhere¹ and consisted of PVK as the photoconductor, C_{60} as the sensitizer, BBP as the plasticizer, and 5CB and AODCST as the nonlinear chromophores (NLO).^{1,12} We studied both unplasticized composites [PVK (99-x%)/ C_{60} (1%)/NLO (x%)], where x varied from 1 to 20 mol % [high T_g ranging between 225 °C for $x=1\%$ and 80 °C for $x=20\%$], and plasticized composites [PVK (99%)/ C_{60} (1%)/BBP (50-y%)/NLO (y%)], where y varied from 1 to 40 mol % (low T_g of ~ 21 –24 °C for all values of y). Sample preparation consisted of the following steps. First, PVK was dissolved in a mixture of toluene and cyclohexanone wt 4:1. Then, C_{60} was dissolved in toluene and added to a solution of PVK. Finally, the dye was added to a solution of PVK and C_{60} . Then we prepared the films on indium-tin-oxide (ITO) slides, sandwiched them together, and baked them in a vacuum oven for 1 h. The thickness of the samples varied from 30 to 70 μm .

We used a mode-locked Ti:sapphire laser pumped with an Ar⁺ laser. At pump power of 6 W, the average output power of the Ti:sapphire laser was ~ 0.5 W. The duration of the pulse was ~ 50 fs, and the wavelength range was ~ 760 –800 nm. The light of fundamental frequency ω was obliquely incident on the sample, and the second harmonic (2ω) 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 fundamental light modulated by a chopper. For polarization measurements, a polarization rotator in front of the sample and a polarizer between the sample and the PMT were used. A filter that blocked the fundamental frequency ω and transmitted the second harmonic signal light of 2ω was placed behind the sample. We verified that sample absorption at 2ω was low enough to ensure that the second harmonic light emanated from at least 1.5 μm of the sample thickness.

The experimental run was as follows. First, with no electric field applied, 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 steady state, the electric field was switched off, and second harmonic decay was observed. The switching time of the power supply was less than 5 ms. This is at least an order of magnitude faster than the orientation times obtained from the EFISHG transients in our composites, but much slower than the instantaneous electronic third order response. Thus, we ensured that our measurements are not artifacts of the equipment, but are, indeed, related to chromophore orientation alone. The experiment was performed at electric fields of typically 5–60 V/ μm .

Taking symmetry into consideration, our system, which under applied electric field is expected to possess $C_{\infty v}$ symmetry, should exhibit only p -polarized second harmonic light.¹⁷ In other words, from four possible combinations of incident and second harmonic (SH) light linear polarizations (p fundamental, p SH; p fundamental, s SH; s fundamental, p SH; 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 that expected.

III. RELATIONSHIP BETWEEN THE ORIENTATIONAL TIME MEASURED IN EFISHG AND FWM

Here Sec. III the orientational response 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.^{18,19} In this model, the dynamics of the orientational distribution function $f(\theta, t)$ are 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 measured by various techniques can be expressed through the n th order moments $\langle \cos^n \theta(t) \rangle$ of the orientational autocorrelation functions (OACFs) $\Phi_n(t)$.¹⁸ 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 $D_1 = 2D$.

Temporal development of the orientationally enhanced diffraction efficiency η , measured in the four-wave mixing (FWM) experiment, can be expressed in terms of constants D_n :⁹

$$\eta \sim \{A_1 [1 - \exp(-D_1 t)] + A_2 [1 - \exp(-D_2 t)]\}^2.$$

Then the orientational dynamics of $\sqrt{\eta}$ are 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 theory assuming that the relation $D_2 = 3D_1$ is valid.

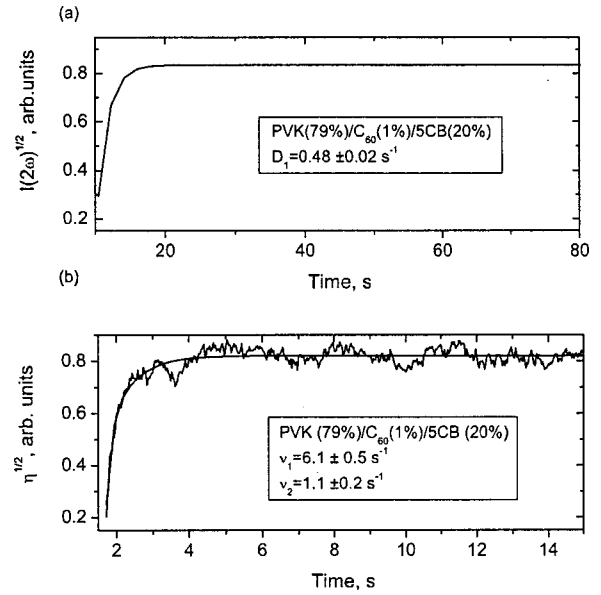


FIG. 1. Example of data analysis for orientational dynamics studies for high- T_g composite (1) at $E_a = 10 \text{ V}/\mu\text{m}$: (a) EFISH signal; (b) FWM dynamics.

The diffraction efficiency dynamics depend on both the photoconductivity and orientational speed. Thus, the orientational contribution is not easily isolated. The rise in diffraction efficiency is often fit to a biexponential function, in which one component of the PR speed is determined by the photoconductivity and the other 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 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 electric fields, that due to projection of the applied field on the grating vector and that of the space-charge field, act upon 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 the rotational diffusion model [Eq. (5)] assume a system of freely rotating dipoles that corresponds to the polymer composite at temperatures above T_g which is the case for our plasticized composites and not the case for the unplasticized ones. Nevertheless, we proceed and believe that reasonable estimates can be made, and that the relationship between EFISHG and FWM orientational dynamics can be established. In any case, we can distinguish the time scales on which 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 composites (1) PVK (79%)/ C_{60} (1%)/5CB (20%) and (2) PVK (49%)/ C_{60} (1%)/BBP (45%)/AODCST (5%) (Figs. 1 and 2). The EFISHG measurements were performed at electric field E_a equal to the projection of electric field applied

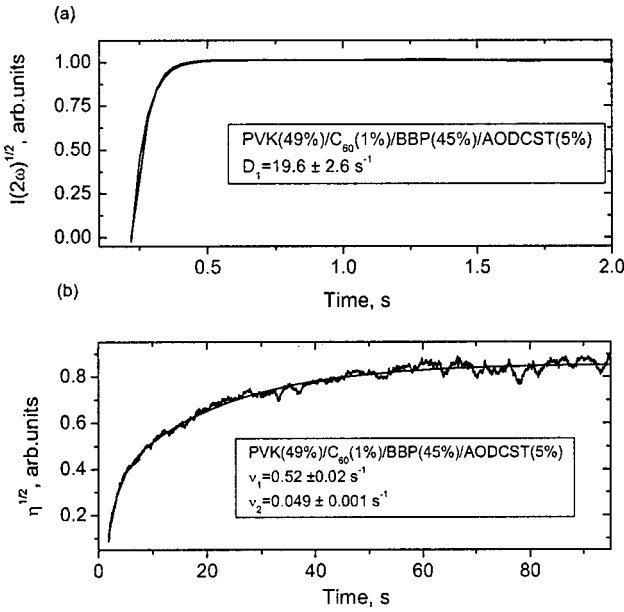


FIG. 2. Example of data analysis for orientational dynamics studies for low- T_g composite (2) at $E_a = 10 \text{ V}/\mu\text{m}$; (a) EFISH signal; (b) FWM dynamics.

on the grating vector \tilde{E}_a in the FWM measurements. Composite (1) is a relatively high T_g composite ($T_g \sim 80^\circ\text{C}$), so at room temperature the chromophore orientation is expected to be slower than that for composite (2) which has $T_g \sim 21^\circ\text{C}$. This is supported by the experimental data: the single exponential fits of $\sqrt{I(2\omega)(t)}$ shown in Figs. 1 and 2 yield coefficients $D_1 = 0.48 \pm 0.02$ and $19 \pm 2.6 \text{ s}^{-1}$, respectively, for these two composites.

Let us now analyze the diffracted signal measured in the FWM experiment. For both composites, we fit the transients $\sqrt{\eta(t)}$ to a biexponential $\sqrt{\eta(t)} \sim [1 - a \exp(-v_1 t) - (1 - a) \exp(-v_2 t)]$. For the transient shown in Fig. 1 [composite PVK (79%)/C₆₀ (1%)/5CB (20%)], the fit yields $v_1 = 6.1 \pm 0.5 \text{ s}^{-1}$ and $v_2 = 1.1 \pm 0.2 \text{ s}^{-1}$. Comparing these constants to orientational constant D_1 for this composite, we conclude that while the faster component v_1 is much larger than the orientational speed $D_1 = 0.48 \text{ s}^{-1}$, the slower component v_2 is rather close. Indeed, the faster component v_1 is found to be intensity dependent and is attributed to photoconductivity.¹ The slower component v_2 is intensity independent and can be attributed to the chromophore orientation. As we discussed above, the average orientational speed measured in the FWM experiment can yield values ranging from D_1 to $D_2 = 3D_1$. The constant $v_2 = 1.1 \text{ s}^{-1}$ fits in the range of $0.48\text{--}1.44 \text{ s}^{-1}$, which confirms it is attributable to orientational.

For the transient shown in Fig. 2 [composite (2)], the $\sqrt{\eta(t)}$ biexponential fit yields $v_1 = 0.52 \pm 0.02 \text{ s}^{-1}$ and $v_2 = 0.049 \pm 0.001 \text{ s}^{-1}$. If one compares these constants to the orientational speed D_1 determined from the EFISHG, one concludes that, since the orientational speed is much higher than both the v_1 and v_2 photorefractive speed components, neither can be attributed to orientation. As our FWM experiments showed, both v_1 and v_2 are intensity dependent and are 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 about which we now report. As discussed in Sec. II A, the intensity of the second harmonic signal measured in EFISHG experiments is quadratic in the electric field [Eq. (4)]. Therefore, this experiment is quite sensitive to changes in the electric field. This allows one to probe the space-charge fields that formed in the material using the EFISHG technique.

Kim *et al.* used second harmonic generation for a space-charge field measurement in a PR crystal LiNbO₃ doped with MgO.²⁰ To our knowledge, similar studies of photorefractive polymers have not been reported in the literature, although an antiguiding waveguide structure was detected with this technique.²¹ As mentioned previously, formation of the photorefractive grating involves different processes that occur in the material under the influence of interfering optical beams. Since originally we set up the EFISHG experiment to probe chromophore reorientation in PR polymer composites, it was reasonable to check whether the presence of light other than that of the Ti:sapphire laser beam used for EFISHG measurements (see Sec. II B) affects orientational processes. In particular, we were interested in how HeNe light of $\lambda = 633 \text{ nm}$ used for our PR measurements influences the chromophore orientational speed measured by EFISHG. So we illuminated our sample with a He-Ne laser beam whose cross section is much larger than that of the Ti:sapphire laser to ensure 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 signal due to chromophores aligning in the electric field. Then, the electric field was turned off, and SH signal decay was observed. Second, the HeNe light was allowed through, and the experiment was repeated in the presence of 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 Fig. 3. We investigated several possible explanations for this.

- (1) 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 and lead 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 direction of polarization of He-Ne light. This would appear as a change in the ratio between the *pp* and *sp* components. This was not observed.
- (2) The effective hyperpolarizabilities, β and γ , changed due to the change in local field in the presence of HeNe light. In Sec. III we established the connection between the intensity $I(2\omega)$ measured in EFISHG and hyperpolarizabilities β and γ [Eq. (4)]. If the hyperpolarizabilities

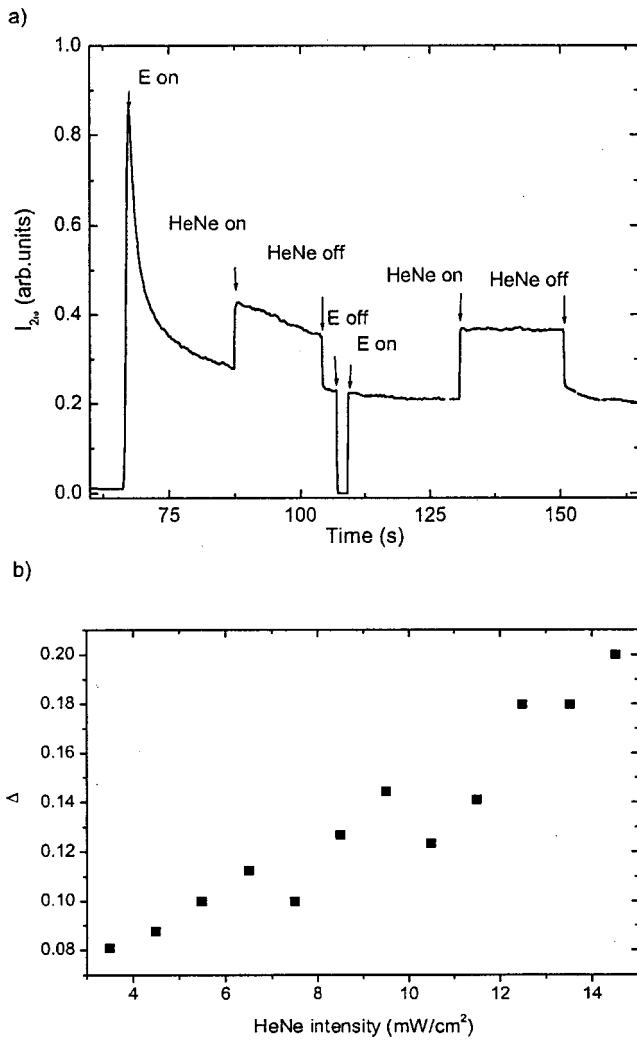


FIG. 3. (a) Influence of HeNe light intensity of 20 mW/cm^2 on the second harmonic signal in composite (2) at $E_0=15 \text{ V}/\mu\text{m}$. (b) (Δ) Incremental increase in SHG intensity as a function of the HeNe light intensity observed in composite (2) at $E_0=10 \text{ V}/\mu\text{m}$.

changed, we would be able to detect changes in the main chromophore absorption peak in the presence of an electric field. No changes in absorption were observed, ruling out this possibility.

- (3) 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 for trap filling with injected charge and non-neutralized ionic buildup at the electrodes, which screen the external electric field.^{1,22} This screening is evident in Fig. 4 as slow decay in the second harmonic intensity shortly after the electric field is switched on. Then, the effective poling field E_{pole} inside the sample is lower than the external field E_0 . When HeNe light is incident, free holes are generated, which then neutralize some of the surface and bulk trapped charge, and consequently increase the internal electric field as observed in Fig. 3(a). Consequently, the screening field is reduced, and the intensity of the second harmonic [$I(2\omega) \sim E_{\text{pole}}^2$] increases.

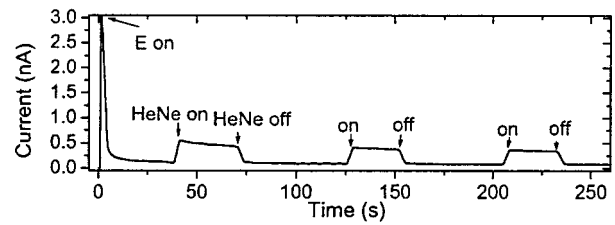


FIG. 4. Poling current in composite (2) at $E_0=15 \text{ V}/\mu\text{m}$. The presence of HeNe light intensity of 10 mW/cm^2 results in a photocurrent which adds to the poling current. The time constant for the rise in current appears to be slower than in Fig. 3(a) due to differences in instrumentation and to the quadratic dependence of SHG on the field applied.

Evidence of 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 composites without a sensitizer (C_{60}) did not exhibit enhancement. We do not believe that C_{60} anions contribute directly to this process since they accumulate very slowly and they do not accumulate in samples containing 5CB due to its high ionization potential, which precludes it from acting as a compensating trap. We did not observe any substantial differences between 5CB and AODCST samples. Also, the effect was not observed in the composites in which the photoconductor poly(*N*-vinylcarbazole) (PVK) was replaced with a nonphotoconductor poly(methyl-methacrylate) (PMMA). In addition, the enhancement increased as a function of the HeNe light intensity [Fig. 3(b)], electric field applied, 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, these composites exhibit high dark current due to ionic impurities that move towards the electrodes and uncompensated for trap filling with injected charge. This is illustrated in Fig. 4, which shows typical poling current dynamics for composite (2). Therefore, in these composites, 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, shown for the highly plasticized (room T_g) composite (2) in Fig. 3, illustrates screening of the external electric field. At time $t=65$ s, the electric field is applied, and the chromophores orient themselves with the inverse time constant (orientational speed) $D_1 \sim 20 \text{ s}^{-1}$. In the meantime, the impurity ions start to move towards the opposite electrodes, and build up, creating an internal field that reduces the total electric field in the sample. This reduction is accompanied by a reduction in the second harmonic signal observed (the peak in Fig. 3). At $t=90$ s, the HeNe light is turned on, partially compensating for 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 for, and the second harmonic intensity is reduced. 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 reappear 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 chromophore reorientation in the low- T_g composite is faster than in the high- T_g composite; this is reflected by the rise in second harmonic generation when the electric field is applied. The diffusion constant deduced 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 is 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 measured in the FWM holographic experiment and in the EFISHG experiment was established.

A simple theoretical relationship between the orientational dynamics 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 chromophore-doped polymers, such as internal electric field formation inside the material and, thus, it can be used as an effective probe of internal electric fields.

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