Third harmonic autocorrelation and wave mixing in a thin film of poly(*p*-phenylenevinylene)

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Abstract: We show here that a thin film of a nonlinear conjugated polymer: poly(*p*-phenylenevinylene) (PPV) is capable of efficiently generating the third harmonic of femtosecond pulses of light at the near infrared (including telecommunication bands) wavelengths, giving coherent, low divergence beams in the visible range. By using more than one fundamental beam overlapping in space and in time on the PPV film, autocorrelation signals are observed as well as higher order mixing signals due to $\chi^{(5)}$ and higher-order nonlinear susceptibilities. These signals can be used for applications such as short laser pulse diagnostics and photonic signal processing and they provide information about the nonlinear properties of the material itself.

OCIS codes: (190.4710) Optical nonlinearities in organic materials; (190.2620) Frequency conversion

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1. Introduction

The phenomenon of third harmonic generation (THG) is a well-known manifestation of the cubic optical nonlinearity of materials, $\chi^{(3)}$. It is generally regarded to be a weak effect, of importance for material characterization [1] or microscopy [2] but of little other practical uses. The efficiency of THG depends on the material nonlinearity, incident light (fundamental) intensity and the length of coherent interaction. High third-order nonlinearities are often reported for various materials, in particular organics [3-5] but the THG efficiencies are limited by other factors. Poly(*p*-phenylenevinylene) belongs to the family of polymers which possess strong π-electron conjugation. This is a crucial factor in attaining high optical nonlinearities, and, indeed, PPV and its derivatives have been considered for applications in which a high value of the nonlinear refractive index, n_2 would be of advantage to obtain all-optical switching of optical signals at relatively low light intensities [6]. Numerous studies reported the values of the third-order susceptibility of PPV for a degenerate process $\chi^{(3)}(\omega;\omega,-\omega,\omega)$ reaching 10^{-9} esu (about 10^{-17} m^2/V^2) [7-9], with the third-harmonic generation related $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ usually quoted [10-13] as being in the range of 10^{-11}-10^{-10} esu (about 10^{-19}-10^{-18} m^2/V^2). With these high nonlinearities one can expect that even thin films may produce strong third-order nonlinear optical effects. This should include efficient third harmonic generation at intensities in the range of gigawatts/cm^2 (the damage threshold for femtosecond pulses for PPV is on the order of 100 GW/cm^2).

We note that the efficiency of the conversion of a fundamental into the third harmonic can be approximated as (cf [14]):

$$\Omega_3 \cong \frac{\omega^2}{n_{3\omega} n_\omega^3 \varepsilon_0^2 c^4} \left|\chi^{(3)}\right|^2 I_\omega^2 L_{eff}{}^2 \qquad (1)$$

where ω is the frequency of the fundamental, n is the refractive index, ε_0 is the vacuum susceptibility, c is the speed of light, I_ω is the incident intensity of a fundamental wave and L_{eff} is the interaction length. The latter can only be equated to the real length of a sample, L, if the absorption of both the fundamental and the harmonic are insignificant and the thickness is less

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than the coherence length l_c. Due to refractive index dispersion, the coherence length for the $\omega+\omega+\omega \mapsto 3\omega$ interaction,

$$l_c = \frac{\lambda}{6(n_{3\omega} - n_{\omega})} \tag{2}$$

is quite short in most solid or liquid materials, on the order of submicron to a few microns [1]. For example, in the extreme case for THG in PPV at about 1.5 micron we estimate l_c=0.38 μm. The phase-matched THG, where the interaction length can be very long, is possible but seldom observed [14-16]. Examination of the parameters in Equation (1) indicates, however, that it should be possible to obtain a reasonably high conversion efficiency even for very short interaction lengths. If a 1 micron thick material with $\chi^{(3)}$ of about $3x10^{-19}$ m^2/V^2 (as for PPV at λ=1.5 μm [13]) is subjected to a short pulse beam with the peak intensity of about 30 GW/cm^2 the efficiency may reach about 0.1%, provided that effects like linear and nonlinear absorption of the fundamental and the harmonic, saturation effects, higher order nonlinear effects and damage do not limit the conversion efficiency. In fact, for materials of PPV type, the main limitation in attaining such and higher THG efficiencies appears to be absorption of the generated THG, which can be shown to limit the interaction length to

$$L_{eff} = 2\frac{1-\exp(-\frac{\alpha L}{2})}{\alpha L} L \cdot \tag{3}$$

For the linear absorption coefficient $\alpha=2x10^5$ cm^{-1} (as in PPV at about 500 nm) the effective length is as short as 0.1 μm.

2. Materials

PPV films used in the THG experiments were prepared according to the precursor polymer route [17-19] in which tetrahydrothiophene was used to react with *α,α'*-dichloro-*p*-xylene to form the *bis*-sulfonium salt monomer. The monomer salt was polymerized in aqueous solution at ~0° C using sodium hydroxide. The viscous polyelectrolyte precursor polymer solution (about 0.5 wt % of the polymer) was purified by dialysis and refrigerated. In order to limit the tendency of the polymer for crystallisation the precursor solution was diluted with methanol (for about 30 wt % of methanol), stored at room temperature for 24 hours then filtered (0.5 μm), and concentrated by evaporation. PPV films were obtained by spinning of the solution of the precursor polymer onto silica or glass microscope slides under nitrogen and thermally converted under dynamic vacuum at elevated temperatures (180-200°C) for 3-5 hours [8,9]. Films were characterised by UV-VIS-NIR spectroscopy, refractive indices and thicknesses were measured with a prism coupler. Absorption spectra of the PPV films showed a maximum at ca. 430-440 nm, the absorption coefficients at the resonance were in the range $(4\text{-}4.6)x10^5$ cm^{-1}. Films were slightly opaque and highly birefringent. For example a 1.09 μm thick film had refractive indices n_{TE} = 2.302 and n_{TM} = 1.614 at 632.8 nm, 2.124 and 1.593 at 810 nm, respectively, that indicated anisotropic alignment of the polymer molecules [7]. The third-order optical nonlinearities of the films, evaluated with 120 fs pulses using degenerate four wave mixing at 800 nm, were in the range $|n_2| = (2\text{-}4)x10^{-12}$ cm^2/W or $|\chi^{(3)}|= (2.5\text{-}5)x10^{-10}$ esu.

3. Results

We find that reasonably strong, easily seen with a naked eye as colour dots on a target screen, third-harmonic beams can be generated in ~1 μm thick films of PPV with the output from an optical parametric amplifier operating in the range 1.2-1.8 μm. The system used by us consisted of a Clark-MXR 2000 Ti-sapphire regenerative amplifier providing 1 kHz 150 fs pulses at 775 nm (up to 1 mJ/pulse) to pump a Light Conversion TOPAS parametric amplifier. Microjoule range pulses from the OPA were attenuated and then weakly focused (about 300 μm spot size) on the surface of a PPV covered silica slide. The third harmonic spot could be easily seen at a target after the sample and its identity as THG could be immediately

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ascertained by tuning the OPA to different wavelengths, which results in the colour of the spot being changed. The colour of the THG can be contrasted with the colour of the bright spot on the PPV film itself which stays yellowish in a wide range of the excitation wavelengths and is mostly due to three-photon induced fluorescence [20]. The three-photon absorption is due to the imaginary part of the fifth-order optical nonlinearity $\chi^{(5)}(\omega;\omega,-\omega,\omega,-\omega,\omega)$ and is apparently a relatively efficient process for PPV within the wavelength range of thrice that of the one-photon absorption band. However, we are not aware of a measurement of the three-photon absorption coefficient of PPV at 1.2-1.8 μm.

An interesting feature of the THG spot on the screen behind the sample is its smaller size compared to that of the fundamental beam spot, indicating that the divergence of the generated beam is smaller than that of the fundamental (cf [21]). This can be understood from considerations of Gaussian beam optics. If the fundamental Gaussian beam is focused to a spot of radius w_0, its divergence angle is [22]

$$\Theta_0 = \frac{2}{\pi}\frac{\lambda}{2w_0}. \tag{4}$$

For the third harmonic, the spot size from which it originates is smaller, due to the fact that the nonlinear polarization is proportional to the cube of the fundamental field amplitude: $w_{0,THG} = w_0/\sqrt{3}$, but $\lambda_{THG} = \lambda/3$, thus the divergence angle of the third harmonic is reduced compared to that of the fundamental: $\Theta_{0,THG} = \Theta_0/\sqrt{3}$.

The THG from a thin film of PPV or a similar material can be exploited for tasks such as laser diagnostics (cf [23,24]). We have, in fact, used the phenomenon as a convenient way of aligning a system for BOXCARS geometry measurement [5,25] of degenerate four-wave mixing. In a BOXCARS geometry there are three beams coincident on the sample, forming three corners of a rectangle on a screen after the sample. Figure 1 shows a scheme of the experiment and the photograph of actual third harmonic spots. The main 10 bright spots seen on the screen are rationalized once one considers the 3ω terms of the following expansion for the nonlinear polarization $\mathbf{P}_{\mathrm{NL}}$:

$$P_{NL} \propto \left[e^{i\omega t-\mathbf{k}_1\mathbf{r}} + e^{i\omega t-\mathbf{k}_2\mathbf{r}} + e^{i\omega t-\mathbf{k}_3\mathbf{r}} + c.c.\right]^3 \tag{5}$$

where $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ are the wavevectors of the three fundamental beams. There are 10 third harmonic terms (and their complex conjugates) in the expansion, each of them characterized by the appropriate wavevector: three corner beams are at $3\mathbf{k}_1$, $3\mathbf{k}_2$ and $3\mathbf{k}_3$, the six mixing signals on the sides of the triangle are $2\mathbf{k}_1+\mathbf{k}_2$, $2\mathbf{k}_2+\mathbf{k}_1$, $2\mathbf{k}_2+\mathbf{k}_3$, $2\mathbf{k}_3+\mathbf{k}_2$, $2\mathbf{k}_3+\mathbf{k}_1$ and $2\mathbf{k}_1+\mathbf{k}_3$ and, finally the spot in the middle of the triangle derives from $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$ mixing of the three beams.

The mixing signals appear only when the beams are coincident on the PPV film within the time corresponding to the pulse duration, thus they can be used for autocorrelation measurements of the pulse width as shown in Fig. 2. Conditions of such an experiment can be optimized for obtaining interferometric autocorrelation, single shot autocorrelation and frequency resolved optical gating (FROG) [23] spectra.

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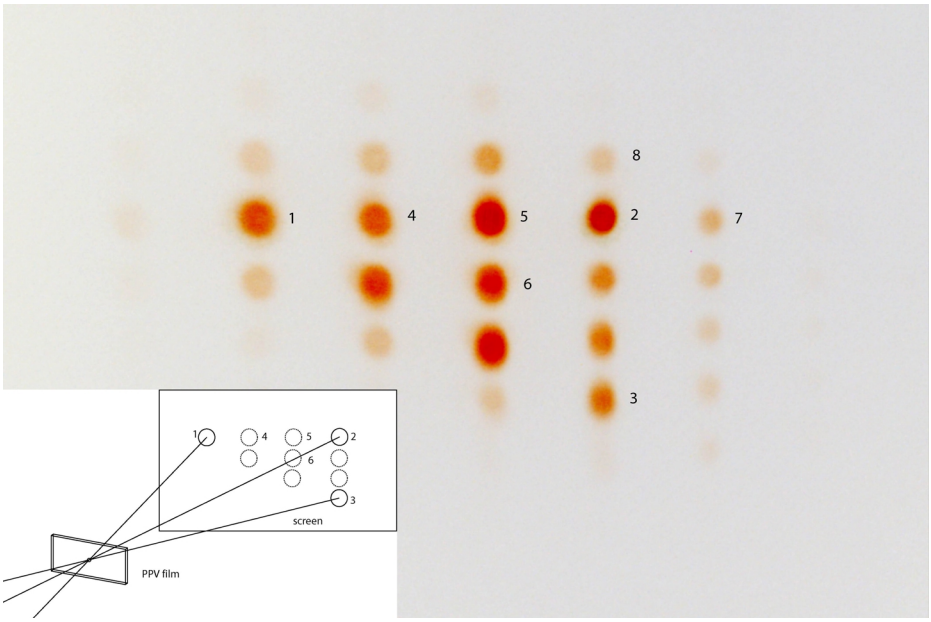

Fig. 1. Third-harmonic wave mixing in a 1 μm thick film of PPV (poly-*p*-phenylenevinylene) observed in a setting analogous to BOXCARS degenerate four-wave mixing (DFWM) geometry. The inset shows scheme of the experiment. The photograph (inverted colour) shows 500 nm spots for the three beams at 1500 nm. 1, 2, and 3 are third harmonic (500 nm) spots ($3\mathbf{k}_1$, $3\mathbf{k}_2$ and $3\mathbf{k}_3$ interactions). Examples of THG mixing are spots 4 and 5 and 6 ($2\mathbf{k}_1+\mathbf{k}_2$. $2\mathbf{k}_2+\mathbf{k}_1$ and $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$ interactions) and spots 7 ($4\mathbf{k}_2-\mathbf{k}_1$) and 8 ($4\mathbf{k}_2-\mathbf{k}_3$) are examples of fifth-order mixing through the $\chi^{(5)}(3\omega;\omega,\omega,\omega,-\omega,\omega)$ susceptibility.

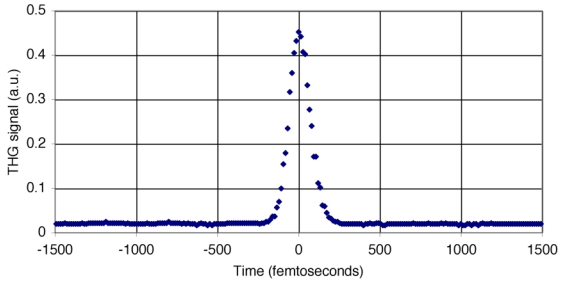

Fig. 2. Third-harmonic autocorrelation signal measured on a PPV film at 1500 nm.

It is evident from Fig. 1 that there are also additional beams being generated that are not due to simple third-harmonic mixing. One can in principle treat the additional spots as originating in diffraction of the third harmonic on the transient grating created by the interference of the fundamental beams in the PPV film. This means that they are due to the superposition of two nonlinear processes: i.e. the degenerate nonlinearity at 1500 nm and the third-harmonic generation. One should note that, as an example, self-diffraction of a THG beam with the wave vector of $3\mathbf{k}_1$ on a grating formed by two fundamental beams at $\mathbf{k}_1$ and $\mathbf{k}_2$, that is with the grating vector of $\mathbf{k}_1-\mathbf{k}_2$, will give a spot at the position determined by the combination $4\mathbf{k}_1-\mathbf{k}_2$. However, a simpler way of predicting where the additional spots will appear exists: one can treat these interactions in terms of higher order nonlinearities. In particular, the strongest diffraction spots should originate from $\chi^{(5)}(-3\omega;\omega,\omega,\omega,-\omega,\omega)$. The number and relative intensities of the signals can be predicted by taking the expansion of the

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fifth power of the sum of all fundamental fields and selecting the terms that oscillate at 3ω. There are 25 such terms, ten of them coinciding with the wavevectors of the simple third harmonic signals considered above and 15 additional ones, separated from them in space.

Figure 3 shows examples how the diffraction signals originate from vector summation of the wavectors of the interacting waves.

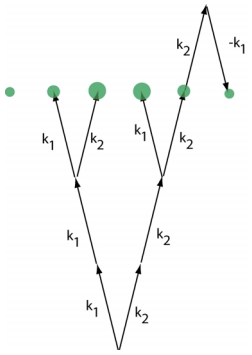

Fig. 3. Scheme of formation of third-harmonic mixing signals due to $\chi^{(3)}$ and due to $\chi^{(5)}$.

The nonlinear susceptibilities responsible for the observed phenomena can be evaluated. Estimates of the THG conversion efficiency (absolute THG powers on the order of a μW at fundamental intensities of 30 GW/cm^2 are typically obtained, leading to conversion efficiencies of 10^{-4}-10^{-3}) indicate that the ranges of values of $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ of the order of 10^{-19}-10^{-18} m^2/V^2 quoted in many papers for PPV are indeed satisfied in our experiments. The existence of additional, higher-order mixing spots provides us with information that can be used for a rough estimation of $|\chi^{(3)}(\omega;\omega,-\omega,\omega)|$ at 1.5 μm as well. We observe about a factor of ten ratio between the intensity of diffraction spots and the third-harmonic mixing spots at power levels of about 50 GW/cm^2 in a 1 μm thick film. Application of Kogelnik diffraction efficiency formula [26],

$$\eta = \sin^2(\pi \frac{L}{\lambda} \Delta n) \tag{6}$$

indicates that a complex refractive index modulation $|\Delta n|$ on the order of 0.1 must have been present in the sample, leading to the nonlinear refractive index of $|n_2|=2\text{x}10^{-12}$ cm^2/W and $|\chi^{(3)}(\omega;\omega,-\omega,\omega)|$ of about $2\text{x}10^{-10}$ esu ($3\text{x}10^{-18}$ m^2/V^2) at 1.5 μm. This is similar to the values determined for PPV at shorter wavelengths [8,9]. Alternatively, one can treat the diffraction as a $\chi^{(5)}$ process. We note that the two approaches are equivalent and that a $\chi^{(5)}$ process can be treated as "cascading" of two cubic processes and $|\chi^{(5)}(3\omega;\omega,-\omega,\omega,\omega,\omega)|$ on the order of 10^{-36} m^4/V^4 can be determined for PPV at 1.5 μm.

In summary, we can state that the observed phenomena provide a good demonstration of the exceptionally high third-order optical nonlinearity available in poly(*p*-phenylenevinylene), can be of importance for laser diagnostics and the effects can be used for investigations of various types of material nonlinearities. The advantage of a THG process giving an upconverted signal in the visible range may also be considered for processing of photonic signals in the telecommunication range of wavelengths. Other materials with exceptionally high $\chi^{(3)}$ may provide an improved efficiency for such applications if linear absorption of the third harmonic can be minimized in the wavelength region of interest.

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