Third-order optical non-linearity in metal-containing organic polymers

C. C. Frazier, S. Guha, W. P. Chen, M. P. Cockerham and P. L. Porter
Martin Marietta Laboratories, 1450 S. Rolling Road, Baltimore, MD 21227, USA

and E. A. Chauchard and Chi H. Lee
Electrical Engineering Department, University of Maryland, College Park, MD 20742, USA

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Many metal-containing polymers have extended conjugation and low-energy spectroscopic charge transfer transitions which can contribute to the electronic processes associated with the manifestation of large third-order optical non-linearities. Third harmonic generation and power limiting experiments have been used to evaluate the third-order susceptibility of the palladium poly-yne $[Pd(PBu_3)_2C_2C_6H_4C_2]_n$. From power limiting experiments, an n_2 (non-linear refractive index) value fifty eight times that for carbon disulphide has been estimated for a 120 μm palladium–poly-yne–polyimide cast film.

(Keywords: non-linear optics; third-order susceptibility; non-linear refractive index; third harmonic generation; power limiting; palladium poly-yne)

INTRODUCTION

Reports of organic macromolecules with large optical non-linearities, substantial damage thresholds, and fast response times have focused attention on organic polymeric materials as potential media for the performance of optical information processing operations and for thin film waveguides for integrated optics applications[1-3]. The structural characteristics that play key roles in generating optical nonlinearity in organic compounds are well known and have been discussed by a number of researchers[4-10]. For the manifestation of large third-order nonlinearities, π-electron delocalization must be present in the molecule, with long conjugated polymeric chains offering an obvious means of realizing this feature[10]. The details of the structure and dynamics of the π-electron distribution will determine the magnitude of the observed third-order non-linearity. For aromatic molecules, the third-order susceptibility ($\chi^{(3)}$) has been shown to be influenced by perturbation of the ring potential and by ring substitution with electron donor and acceptor groups[9]. Charge transfer interactions which influence the π-electron distribution may also be presumed to have a significant effect on modulating $\chi^{(3)}$.

To date, purely organic compounds have received almost all of the emphasis in the search for macromolecular systems with large third-order susceptibilities. However, many organometallic polymers also have extended π-electron delocalization plus additional features which may be of value in enhancing $\chi^{(3)}$. Linear transition metal-containing organic polymers have repeating units where the transition metal(s) is incorporated in such a way that some transition metal d-orbitals interact with the conjugated π-electron orbitals of the organic moiety of the repeating unit. This provides an extended, delocalized electronic system within the polymer chain. Furthermore, the detailed electronic features of the polymer can be manipulated by varying the type of ligands attached to the metal centres. Additionally, many organometallic polymers have low-lying charge transfer transitions not found in organics, e.g. metal-to-ligand charge transfers (MLCT) and ligand-to-metal charge transfers (LMCT), which are associated with significant reordering of the π-electron distribution[11].

We have initiated a study of metal-containing organic polymers by examining the transition metal poly-yne series first synthesized by Hagihara, Sonogashira and Takahashi[12]. Many of these rigid-rod, conjugated organometallic polymers are lyotropic liquid crystals and have been shown to respond to magnetic and electrical fields[13]. Although the use of these compounds for nonlinear optical applications has not been previously suggested, their structural and physical properties (including low-energy MLCT transitions) should lead to the manifestation of large third-order optical non-linearities both as lyotropic solutions and as cast films.

EXPERIMENTAL

The palladium poly-yne utilized for third harmonic generation and power-limiting experiments was prepared according to the procedure outlined in ref. 14. The polymer fraction used to prepare solutions and cast films had an average molecular weight of 32 000 amu, as determined by calibrated high-pressure liquid chromatography. The palladium poly-yne film used in power limiting experiments was formed from a solution of the palladium polymer and Upjohn polyimide 2080D in 1-methyl-2-pyrrolidinone. This solution was spread on a glass plate using a doctor blade, and the solvent was removed from the resulting thin film by placing the plate in a vacuum oven at room temperature for a period of five

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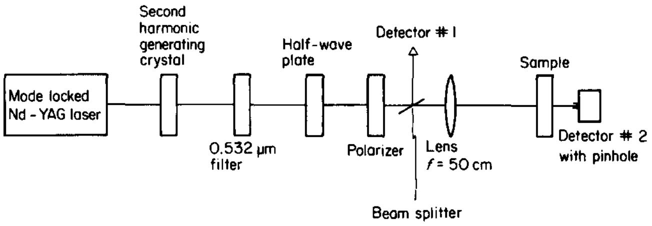

Figure 1 Experimental arrangement

to twenty-four hours. Dry free-standing films with thicknesses of 25–120 μm were easily prepared.

Third harmonic measurements were obtained using a mode-locked Nd:YAG laser with a pulse train of 10 pulses of 125 ps duration each. The experimental arrangement involved a reference and sample chamber and is similar to the second harmonic experiment some of us have previously described[15].

Power limiting experiments employed the experimental arrangement shown in *Figure 1*. Single pulses of 1.06 μm radiation obtained from a passively mode-locked Nd:YAG laser operating at 1 Hz were frequency doubled. The resulting 0.532 μm radiation (pulse width 90 ps) was passed through a variable attenuator consisting of a half-wave-plate and polarizer combination. The maximum energy available at 0.532 μm was approximately 1 mJ. The beam was focused by a 50 cm focal length lens to a spot size of 117 μm radius (half-width at e^{-1} of maximum). The sample (film) was placed at the focus and a detector (D_2) with a pinhole of 25 μm diameter, placed 1 cm away from the sample, measured the transmitted fluence. Part of the incident beam was deflected by a microscope slide used as a beam splitter. The energy of this beam, measured by detector D_1, was used to monitor the amount of energy incident on the sample. D_1 and D_2 were calibrated pyroelectric detectors (Laser Precision, RjP735).

RESULTS AND DISCUSSION

Third-harmonic generation in liquid solutions of a metal poly-yne

Bey, Giuliani and Rabin have derived the following expression to represent the intensity of third harmonic radiation generated in an isotropic non-linear medium[16]:

$$I_{3\omega} \propto \frac{\chi^{(3)^2}[e^{-3\alpha_1 l} + e^{-\alpha_3 l} - 2e^{-1/2(3\alpha_1 + \alpha_3)l}\cos(\Delta k)l]}{(\Delta k)^2 + [1/2(\alpha_3 - 3\alpha_1)]^2}$$

where

α_1 = linear absorption coefficient at the fundamental frequency;
α_3 = linear absorption coefficient at the third harmonic frequency;
l = cell length;
$\chi^{(3)}$ = non-vanishing component of the fourth rank electric susceptibility tensor;
$\Delta k = k_3 - 3k_1$, the real part of the wavenumber mismatch.

When $\alpha_3 \gg \alpha_1$, as is the case for the solutions examined in this work, the above expression reduces to

$$I_{3\omega} \propto \frac{\chi^{(3)^2} e^{-(3\alpha_1 l)}}{(\Delta k)^2 + (\frac{1}{2}\alpha_3)^2}$$

The susceptibility $\chi^{(3)}$ is obtained from the relationship

$$\chi^{(3)} = L^4[N_0(\gamma_0) + N(\gamma)]$$

where

L = Lorentz local field factor;
N_0 = concentration of solvent molecules;
γ_0 = hyperpolarizability of solvent molecules;
N = concentration of the solute (polymer repeating unit);
γ = hyperpolarizability of solute (polymer repeating unit).

Hermann has used these relationships to derive the hyperpolarizabilities and phase-matching characteristics of a series of cyanine dyes[17]. In this study, a similar treatment with the palladium polymer,

$$[\mathrm{Pd(PBu_3)_2{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C}]_n$$

leads to a hyperpolarizability value of 1.47×10^{-33} esu for the metal–poly-yne repeating unit in benzene. *Figure 2* shows the experimental points and calculated values using the above hyperpolarizability value. The solid line is the calculated curve and the open circles are experimental data. The good agreement between the experimental and calculated values (with constant refractive indexes) strongly suggests that within the examined concentration range and for this solvent, phase-matching is not significant and can be ignored in these calculations.

The hyperpolarizability value obtained for the palladium–poly-yne is not a nonresonant parameter since the generated third harmonic (355 nm) is near λ_{max} (344 nm) of the metal–ligand charge transfer of the metal–poly-yne. Experiments designed to measure the nonresonant hyperpolarizability of a series of metal poly-ynes by means of four-wave-mixing are in progress.

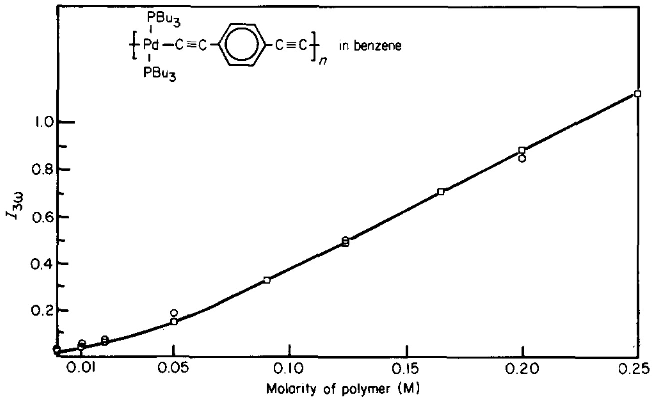

Figure 2 Variation of third harmonic signal *versus* molarity of palladium poly-yne in benzene solutions where □ = calculated values and ○ = experimental points

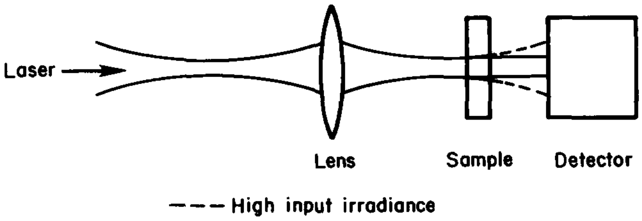

Figure 3 Non-linear transmission measurement set-up

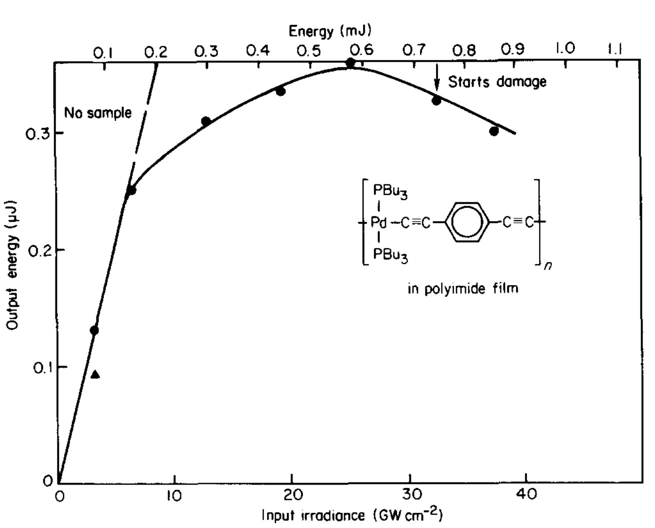

Figure 4 Power limiting data for 120 μm palladium–poly-yne–polyimide cast film where △ = transmission after exposure to high input irradiance

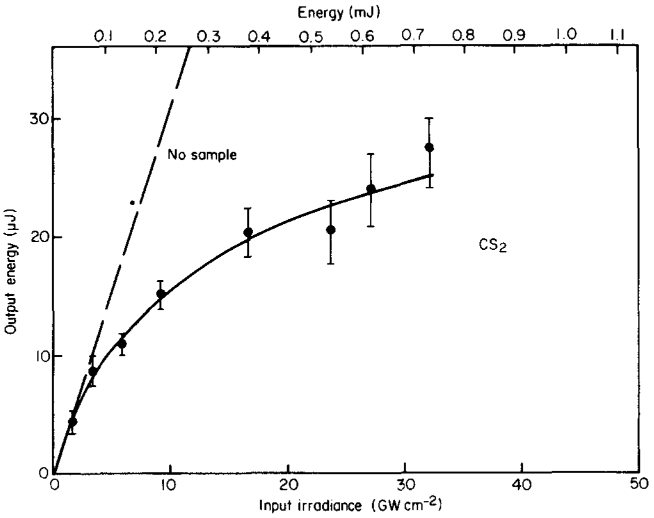

Figure 5 Power limiting data for 1 cm pathlength of carbon disulphide

Direct estimate of n_2 *(non-linear refractive index) in polymer films*

The power limiting method was chosen to estimate n_2 in polymeric films[18]. *Figure 3* provides a simplified explanation of the technique. For a range of low incident energies on a sample, the energy transmitted through the sample increases linearly with increasing incident energy. For non-linear samples, the transmitted energy begins to level off above a specific incident energy and becomes independent of the incident energy (thus, power limiting). The basis for this behaviour lies in the response of non-linear materials to high-intensity Gaussian beams. Under these conditions, the nonlinear medium acts, depending on the sign of n_2, either as a diverging (as shown in *Figure 3*) or converging lens.

For low incident energies on the palladium–poly-yne film ($\sim$0.2 M Pd–polymer repeating unit), the readings at D_2 increased with D_1 (*Figure 4*). At incident energies of about 200 μJ, the film's non-linearity is expressed, and the reading at D_2 becomes approximately independent of the incident energy. At an energy of $\sim$0.75 mJ (irradiance of 33 GW cm^2), the film starts to be damaged, i.e. the surface blackens and the film fails to return to the original high transmission state at low irradiance.

To assign an n_2 (non-linear refractive index) value to the film, we repeated the experiment by replacing the film with a 1 cm cuvette of carbon disulphide (a well-studied non-linear optical material) but keeping the same optical arrangement. As shown in *Figure 5*, power limiting similar to that seen with the film was observed beginning at $\sim$140 μJ. Assuming that external self-action is the mechanistic origin of the power limiting (two-photon or other non-linear absorptive phenomena, while unlikely, cannot be totally excluded at this time) the limiting power is approximately inversely proportional to the irradiance-dependent phase change ($\Delta\phi$) that the laser beam experiences in traversing the non-linear medium. $\Delta\phi$ in turn is proportional to the product of n_2 and sample thickness. Thus, for the palladium–poly-yne–polyimide film thickness of 120 μm, an n_2 value of $(140/200) \times (1\,\mathrm{cm}/0.0120\,\mathrm{cm}) = 58$ times that of carbon disulphide is estimated.

CONCLUSIONS

Our original thesis that metal-containing organic polymers should exhibit large third-order susceptibilities is supported by the third harmonic and power limiting experiments described in this paper. Future work in our laboratories will focus on the development of a detailed structure–property relationship for metal–poly-ynes which includes analysis of metal, ligand, and molecular weight variations. Other metal-containing organic polymers (especially rigid-rod polymers) should also have considerable potential as non-linear optical materials.

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