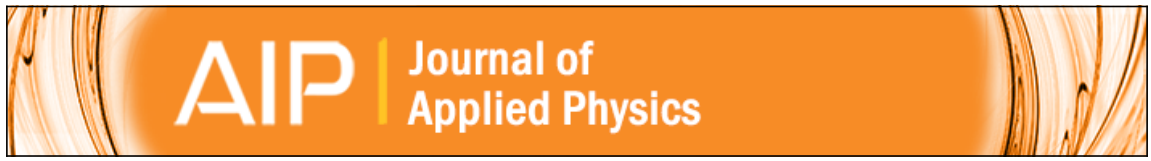

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Nonresonant third-order optical response of polyphenyl acetylene

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Optical phase conjugation by degenerate four-wave mixing in samples of pristine and iodine-doped polyphenylacetylene at ruby laser wavelength (694.3 nm) is reported here. The nonresonant values of the third-order optical susceptibility $\chi^{(3)}$ are determined from the measurements of reflectivity of phase conjugate signals.

I. INTRODUCTION

Polymeric materials have gained immense importance in the last few years due to their attractive nonlinear optical properties.[1-3] Large values of the third-order nonlinear optical susceptibility $\chi^{(3)}$ have been found in many conjugated polymers. The parameter $\chi^{(3)}$ is indicative of the efficiency of a material for optical device applications.[4] Its value can be determined from degenerate four-wave mixing (DFWM) experiments.

In a recent paper[5] we reported our first results of nanosecond DFWM experiments in dilute solutions of polyphenyl acetylene (PPA) at a wavelength of 532 nm given by a doubled Nd:YAG laser. In this paper we present the results of investigations on pristine and iodine-doped PPA at a wavelength of 694.3 nm and at higher power levels of radiation from a ruby laser.

Iodine doping introduces charges on the polymer chain and makes it a better electrical and photo conductor. The electronic absorption is negligible at this wavelength for both undoped and iodine-doped PPA indicating a nonresonant regime. Apart from solutions, evaporated films of these samples are also studied and $\chi^{(3)}$ is determined from the values of phase conjugate reflectivity measured in a DFWM experiment.

II. EXPERIMENTAL PROCEDURE

The PPA used in the present work is thermally polymerized[6] with (mesitylene) Mo $(CO)_3$. The molecular weight of the polymer is 12 000. The x-ray powder diffractogram reveals an amorphous nature. PPA dissolves in many organic solvents at room temperature and possesses the added advantage of air insensitivity. Dilute solutions ($\simeq 10^{-3}$ g/ml) of this polymer are studied in the solvent 1,2 dibromoethane. Homogeneous doping of iodine is done in solution. Thin films of the sample are prepared by slow evaporation of the solution on 2-mm-thick silica substrates.

The optical absorption spectra are recorded on a Hitachi model U-3400 uv-VIS-ir spectrophotometer. These absorption spectra are shown in Fig. 1 for solutions of pure and iodine-doped PPA (50% by weight of iodine in PPA) taken in 1-mm-thick quartz cuvettes. The absorption spectra of thin films of pristine PPA with increasing amounts of evaporated material are shown for comparison in Fig. 2. From Figs. 1 and 2 it is clear that the absorption is negligible at 694.3 nm.

In the experiments of DFWM,[7,8] three input optical beams with electric fields $\mathbf{E}_1$, $\mathbf{E}_2$, and $\mathbf{E}_3$, and respective wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$, all at the same frequency ω interact in the optically nonlinear medium. The third-order nonlinear polarization of frequency ω generated at position $\mathbf{r}$ is given by

$$\mathbf{P}_i^{(3)}(\omega,\mathbf{r}) = \sum_{jkl} 6\chi_{ijkl}^{(3)}(-\omega;\omega,\omega,-\omega) \times \mathbf{E}_{1,j}(\omega,\mathbf{r})\mathbf{E}_{2,k}(\omega,\mathbf{r})\mathbf{E}_{3,l}^{*}(\omega,\mathbf{r}) \times \exp[i(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3)\cdot\mathbf{r} - i\omega t], \quad (1)$$

where $\chi_{ijkl}^{(3)}$ are the tensor components of the third-order susceptibility. The measurement of the coherent output field $\mathbf{E}_4$ generated due to $\mathbf{P}^{(3)}$ at known input fields $\mathbf{E}_1$, $\mathbf{E}_2$, and $\mathbf{E}_3$ with specific polarizations j, k, l gives the different coefficients of the $\chi^{(3)}$ tensor. In the present work, only the component $\chi_{1111}^{(3)}$ of the $\chi^{(3)}$ tensor is determined since all the beams incident on the medium are polarized in the same direction.

Figure 3 depicts the self-phase-matched DFWM setup used in the present work. The two pump beams with electric fields $\mathbf{E}_1$ and $\mathbf{E}_2$ are counterpropagating ($\mathbf{k}_1 = -\mathbf{k}_2$) and the probe field $\mathbf{E}_3$ is incident at a small angle of 5° to $\mathbf{E}_1$. The phase conjugate field $\mathbf{E}_4$ propagating with $\mathbf{k}_4 = -\mathbf{k}_3$, is the time-reversed replica of $\mathbf{E}_3$. In the nonresonant regime, the intensity I_4 of the phase conjugate beam is given in terms of the interaction length d, pump beam intensities I_1 and I_2, and probe beam intensity I_3 as follows:

$$I_4 \propto \frac{(\chi^{(3)})^2 d^2 I_1 I_2 I_3}{n_0^4}. \quad (2)$$

ω is the angular frequency of the laser radiation and n_0 is the linear refractive index of the medium.

The Q-switched ruby laser (RL) (System 2000, JK lasers) gives 20-ns pulses in single-shot operation. Since the output is a diverging beam, a lens (L_1) of 1 m focal length is used for collimation. A retroreflection geometry is employed to get the second pump beam. Mirror M has a

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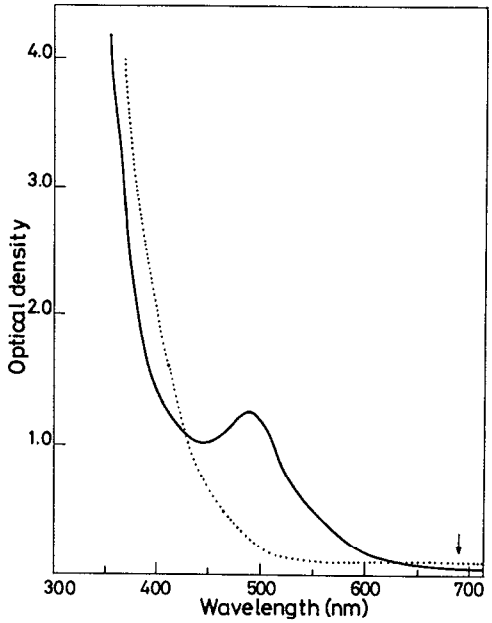

FIG. 1. Optical-absorption spectra of PPA solutions: The dotted line is for undoped PPA and the solid line for 50 wt. % iodine in PPA.

reflectivity of 33% at 694 nm and is mounted on a translation stage. BS_1 with a reflectivity of 18% and BS_2 with a reflectivity of 40% serve as beam splitters. D_1 and D_2 are pyroelectric detectors (model Rjp-735, Laser Precision Corporation), EM is the energy meter (model Rj-7200, Laser Precision Corporation), and S is the nonlinear material. A_1, A_2, and A_3 are suitable apertures. A good spatial and temporal overlap of all the three input beams is ensured at the position of the sample. The phase conjugate reflectivity (I_4/I_3) is measured as a function of (i) the intensity of pump waves and (ii) the weight percent of dopant iodine (5, 10, 20, 40, and 60 wt. %). The phase conjugate reflectivity is measured in CS_2 under identical experimental conditions to estimate the value of $\chi^{(3)}$ in our samples in comparison to that of CS_2 taken as the standard.

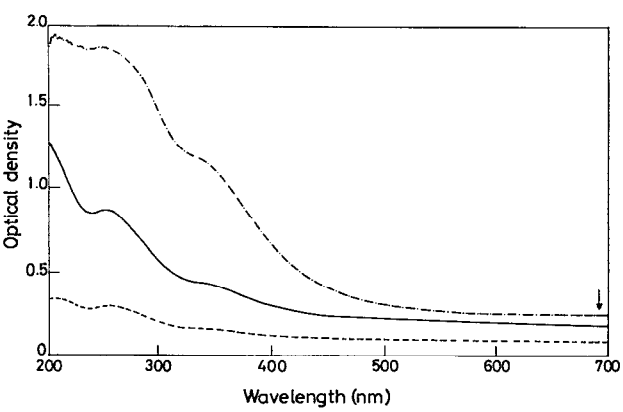

FIG. 2. Optical-absorption spectra of evaporated films of undoped PPA.

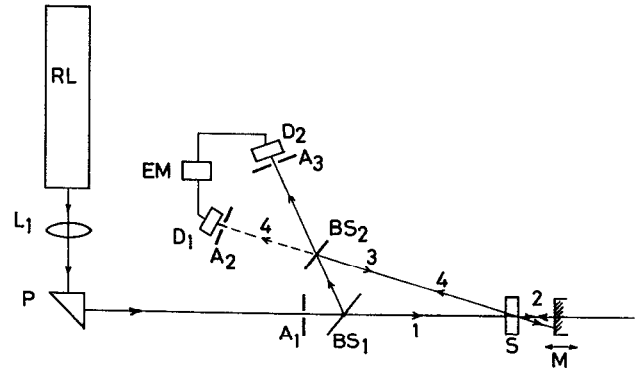

FIG. 3. Experimental arrangement for DFWM.

III. RESULTS AND DISCUSSION

Figure 4 shows the variation of phase conjugate reflectivity as a function of power density of pump 1 (I_1 in MW/cm^2), for both pristine and iodine-doped PPA. The different doping levels are indicated. The pump energy at the maximum I_1 shown here is 150 mJ. It is seen that low doping levels up to 5% do not enhance the reflectivity. Between 5 and 20 wt. % of iodine doping, the reflectivity values show an increase over that for the pristine sample, but a reduction is observed at doping levels in excess of 20 wt. %. This is similar to our observations in Ref. 5 at 532 nm on the same polymer. But unlike in the earlier work, the solvent also gives measurable values of DFWM signal at the ruby laser wavelength.

Since all the samples studied here have negligible absorption at the laser operating wavelength, Eq. (2) is used for determining $\chi^{(3)}$ from the measured values of I_4 in the sample and CS_2 and using the known value of $\chi^{(3)}_{CS_2} = 5.1 \times 10^{-13}$ esu (7.1×10^{-21} m^2/V^2). The refractive indices of CS_2 and the polymer samples are measured at 694 nm using an Abbe refractometer. The values are: 1.628 for CS_2, 1.545 for undoped PPA as well as 5-wt. % iodine-doped PPA, and 1.546 for higher dopant concentrations of iodine in PPA.

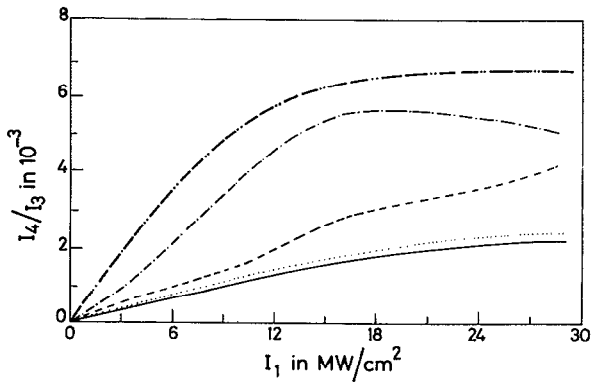

FIG. 4. Phase conjugate reflectivity as a function of pump beam power density. (—): undoped PPA; (....): 5 wt. % iodine; (- - -): 10 wt. % iodine; (--·--·--): 20 wt. % iodine; (-·-·-): 40 wt. % iodine-doped PPA.

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TABLE I. Third order susceptibility of pure and doped PPA.

Material	$\chi^{(3)}$ in 10^{-20} m^2/V^2
Pure PPA	1.70
Iodine-doped PPA	
5%	1.91
10%	2.49
20%	3.21
40%	2.74
60%	2.74

Table I presents the values of $\chi^{(3)}$ determined after accounting for the contribution of the solvent. In the experiments at 532 nm, an enhancement by two orders of magnitude due to doping was noticed. In contrast, doping gives only a marginal improvement at the wavelength 694.3 nm. The doped samples have relatively higher absorption at 532 nm while both pristine and iodine-doped samples have negligible absorption at 694.3 nm. This clearly indicates the role of resonant excitation at 532 nm.

There is an increase in the value of $\chi^{(3)}$ on doping up to 20 wt. %, and above that a fall with a saturation suggesting the saturation of the optical nonlinearity induced by charge-transfer doping of the conjugated polymer. The value of $\chi^{(3)}$ obtained here (1.70×10^{-20} m^2/V^2) for PPA is comparable to the value (2.21×10^{-20} m^2/V^2) estimated on the basis of a one-dimensional pseudopotential model[9–11] where the effects of π-electron delocalization on increased polarizability are demonstrated.

The relatively lower values of $\chi^{(3)}$ in PPA as compared to many other known conjugated polymers is due to the lower levels of conjugation in PPA evident from its absorption spectrum. For linear polyenes, the conjugation lengths can be known[12] from their absorption maxima. The conjugation length for the samples in the present work is only $\simeq 5$ repeat units or 10 carbon double bonds compared to near-infinite conjugation lengths in some polydiacetylenes. The coiled nature of this polymer and the steric interaction of the phenyl groups on the chain limit the high values of $\chi^{(3)}$ possible for one-dimensional conjugated polymers.

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