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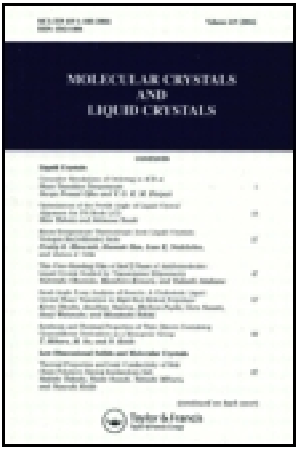

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Third-Order Nonlinear Optical Properties of Substituted Polyphenylacetylenes

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THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF SUBSTITUTED POLYPHENYLACETYLENES

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Abstract Third-order harmonic generation (THG) and electroabsorption (EA) in substituted polyphenylacetylenes (PPAs) which are examples of one-dimensional π-conjugated polymeric systems have been studied. The values of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ obtained from THG measurement for substituted PPAs increase with increasing λ_{max} of absorption. The dispersion of $\chi^{(3)}(-\omega;\omega,0,0)$ for PPA film derived from Kramers-Kronig transformation of optical absorption change under the electric field (EA spectra) has been observed, and it shows the similar shape of the second derivative of the optical absorption spectra. The typical value of $\chi^{(3)}(-\omega;\omega,0,0)$ for *o*-substituted PPA was determined to be *ca.* 10^{-11} esu.

INTRODUCTION

Recently the requirement of novel organic materials which have large optical nonlinearities and ultrafast responses has increased for the development of optoelectronic devices. The intramolecular charge transfer through π-electron conjugation gives large nonlinearities on the molecular level, that is, the third-order optical nonlinearity $\chi^{(3)}_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$ depends on the microscopic third-order susceptibility $\gamma_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$ of the constituent molecular unit. In conjugated linear chain structures such as polyenes, π-electrons are delocalized in their motion only in one dimension along the chain axis[1]. Major contribution to γ_{ijkl} is the chain axis component γ_{xxxx} along the chain axis (x-axis), and hence the averaged susceptibility $<\gamma>$ in isotropic media equals to one-fifth of γ_{xxxx}. There have been various theoretical and experimental studies on linear chain structures [2]. For example, a power law dependence of γ_{xxxx} for linear polyenes has been found on the number of carbon atom sites with exponents of 5.4 for the *trans* and 4.7 for the *cis* conformer, respectively, and it has also been found that γ_{xxxx} is more sensitive to the physical length of the chain than to the conformation[3].

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Off resonant third order optical susceptibility $\chi^{(3)}{}_{1111}(-3\omega;\ \omega,\omega,\omega)$ determined by third harmonic generation (THG) is directly related to $<\gamma>$ of the conjugated compound through local field factors f expressed in terms of the refractive indices n_ω and $n_{3\omega}$ as

$$\chi^{(3)}_{1111}(-3\omega;\omega,\omega,\omega) = Nf_{3\omega}f_\omega f_\omega f_\omega\langle\gamma\rangle(-3\omega;\omega,\omega,\omega), \tag{1}$$

where N is the number of molecules per unit volume. We have focused our researches for long on the development of one-dimensional conducting polymer systems such as polythiophene derivatives and polydiacetylenes and of two-dimensional macrocyclic conjugated compounds such as annulenes and metallophthalocyanine derivatives[4]. In this paper we will discuss another type of one-dimensional π-conjugated system, poly-phenylacetylenes, in the shade of molecular structure and nonlinear optical properties.

Unlike polyacetylene, substituted polyacetylenes such as polyphenylacetylene (PPA) possess high molecular weight over $1\text{x}10^6$, dissolve in various organic solvents, and are considerably thermally stable. The substituted PPAs have alternating double bonds along the main chain and their optical properties can be controlled by introduc-ing bulky groups as a substituent of a phenyl group. The pioneering works on the nonlinear optical properties of substituted PPAs were done by Neher et al[5]. They reported resonant values of $\chi^{(3)}(-3\omega;\ \omega,\omega,\omega)$ up to 10^{-11} esu and $\chi^{(3)}(-\omega;\ \omega,-\omega,\omega)$ of more than 10^{-9}esu with ultrafast responses, and also discussed the direct two-photon interaction with the absorption band. Vijaya et al[6] reported the nonresonant third-order optical responses in pristine and iodine-doped PPA thin films by means of the phase conjugation measured in a degenerated four wave mixing (DFWM) experiment. We have applied soluble substituted PPAs to nonlinear optical waveguide devices based on third-order nonlinear optical effects. In this paper we examined third-order nonlinear optical responses of thin films of various substituted PPAs.

EXPERIMENTAL

Samples

PPAs were synthesized using W, Mo, Nb, and Ta catalysts. Substituted PPA with, say, trimethylsilyl ($-Me_3Si$) and dimethylphenylsilyl ($-Me_2PhSi$) group at *ortho*-position, shows good solubility and film-forming properties. Polydiphenylacetylene (PDPA) derivatives were also synthesized in good yields with $TaCl_5$-cocatalyst

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systems. When a bulky substituent is introduced into one phenyl group of diphenylacetylene, the substituted PDPA becomes well soluble to organic solvents. The details of synthetic procedures were reported elsewhere[7]. Thin films about 0.1 μm thick were prepared on a fused silica substrate by spin-coating of $CHCl_3$ solution.

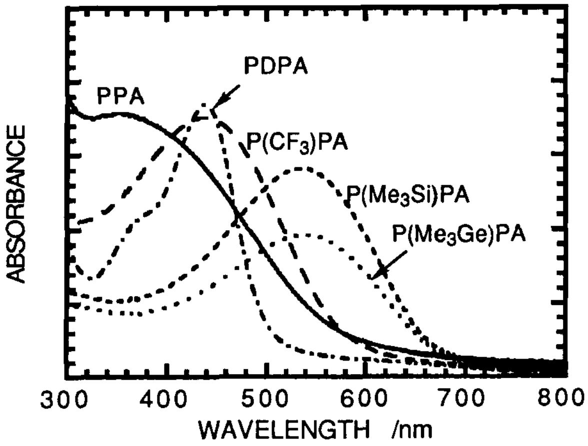


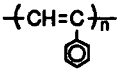
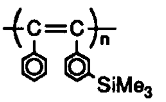
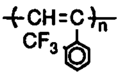
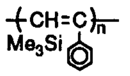
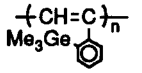
Figure 1 Absorption spectra of substituted polyphenylacetylene thin films. (Chemical structures are shown Table I).

As shown in Figure 1, the electronic absorption of PPA has broad tail with λ_{max} around 352 nm. The absorption of *o*-substituted PPAs shows a red shift with increasing the bulkiness of a substituent group. On the other hand, PDPAs have two absorption maxima; *e.g.*, poly[1-phenyl-2-[*m*-(trimethylsilyl)phenyl] acetylene] shows absorption maxima at 370 and 440 nm with a sharp edge.

Third Harmonic Generation (THG) Measurements

THG measurements were carried out at fundamental wavelength of 1907 nm in a vacuum of several Torr to eliminate the effect of air. The THG Maker fringe pattern was obtained by rotating the film sample. The optical layout has been described in detail elsewhere[8]. Among 8 PPAs and 6 PDPAs, we selected 5 samples as listed in Table 1 for THG measurements.

Table I Linear and nonlinear optical properties of substituted polyphenyl-acetylene thin films.

Polymer		λ_{max} (nm)	$^{*}\chi^{(3)}$ (-3ω;ω,ω,ω) (esu)
PPA		352	5.4×10^{-13}
PDPA		440	8.8×10^{-13}
P(CF$_3$)PA		439	3.0×10^{-12}
P(Me$_3$Si)PA		536	1.7×10^{-11}
P(Me$_3$Ge)PA		548	2.6×10^{-11}

* Fused Silica $\chi^{(3)} = 1.4 \times 10^{-14}$ esu at 1907 nm

Electroabsorption (EA) Measurement

Several researchers have performed electroabsorption (EA) experiments on molecular crystals such as tetracene, single crystals of the conjugated polymer and polyacetylene film. The modulation spectra were related to the first and second derivatives of unperturbed absorption spectra and scaled quadratically with the applied field. If the thickness of the sample is known, we can obtain from EA spectrum the values of Δα (and hence Δk) as a function of wavelength. Through Kramers-Kronig (K-K) analysis, the changes in the real part of the index of refraction Δn can be calculated:

$$\Delta n(\omega) = \frac{c}{\pi} P \int_0^{\infty} \frac{\Delta\alpha}{\omega'^2 - \omega^2} d\omega', \qquad (2)$$

where P denotes the principal value of the integral, and ω and ω' are wavenumbers (cm^{-1}). The measuring system of EA spectrum consists of a grating monochromator with a tungsten-halogen light source and appropriate filters to prevent second-order light from reaching the sample (Figure 2). Thin polymer films were formed on the ITO substrate by spin-coating and then coated with semi-transparent gold electrode by vacuum deposition. A sinusoidal wave (frequency f=1 kHz) with about 10^6 V/cm was

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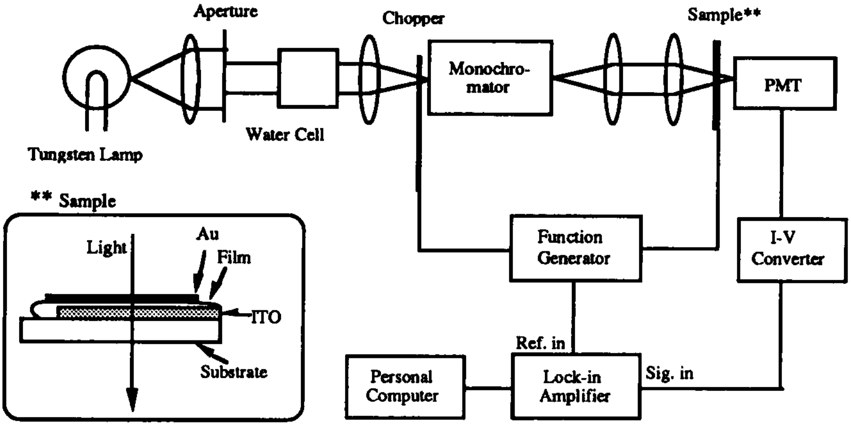

Figure 2 Experimental set-up for electroabsorption spectrum.

applied parallel to the sample surfaces. The modulated signals were detected at the second harmonic frequency 2*f* by means of a conventional lock-in technique. Signals at the fundamental frequency *f* were disregarded as erroneous ones since no linear Stark effect was expected for centrosymmetric amorphous PPA films.

RESULTS AND DISCUSSION

Third Harmonic Generation

The rotational THG Maker fringes were analyzed by standard procedures[9]. The TH intensity $I_{3\omega}$ in an absorbing media is given as

$$I_{3\omega} = \left(64\pi^4 / c^2\right)\left[A\chi^{(3)}\right]^2 I_{\omega}^3 f_a, \tag{3}$$

where I_ω is the light intensity for fundamental frequency, c the velocity of light, A the factor arising from transmission and boundary conditions, and f_a is the absorption dependent factor:

$$f_a = \frac{\left\{\left[1-\exp(-\alpha_{3\omega} d/2)\right]^2 + (\Delta\Psi)^2 \exp(-\alpha_{3\omega} d/2)\right\}}{\left[\left(n_{3\omega}^2 - n_{\omega}^2 - k_{3\omega}^2\right)^2 + \left(2n_{3\omega}k_{3\omega}\right)^2\right]}, \tag{4}$$

where n and k are, respectively, the real and imaginary parts of refractive indices, α the linear absorption coefficient, d the sample thickness and $\Delta\Psi$ the phase mismatch between the fundamental and harmonic frequencies. On the other hand, the TH intensity in a non-absorbing media is given as

$$I_{3\omega} = \left(256\pi^4 / c^2\right)\left[A^*\chi^{(3)} / \left(n_\omega^2 - n_{3\omega}^2\right)\right]^2 I_\omega^3 \sin^2(\Delta\Psi / 2), \tag{5}$$

where A* is an over-all transmission factor. From the curve fitting method the $\chi^{(3)}$ value of fused silica can be confirmed ($1.40\text{x}10^{-14}$ esu at 1907 nm[10]).

Figure 3 shows the curve fitting of Maker fringes for typical samples of PPA and *o*-substituted PPAs. The values of $\chi^{(3)}(-3\omega;\ \omega,\omega,\omega)$ for substituted PPAs increase

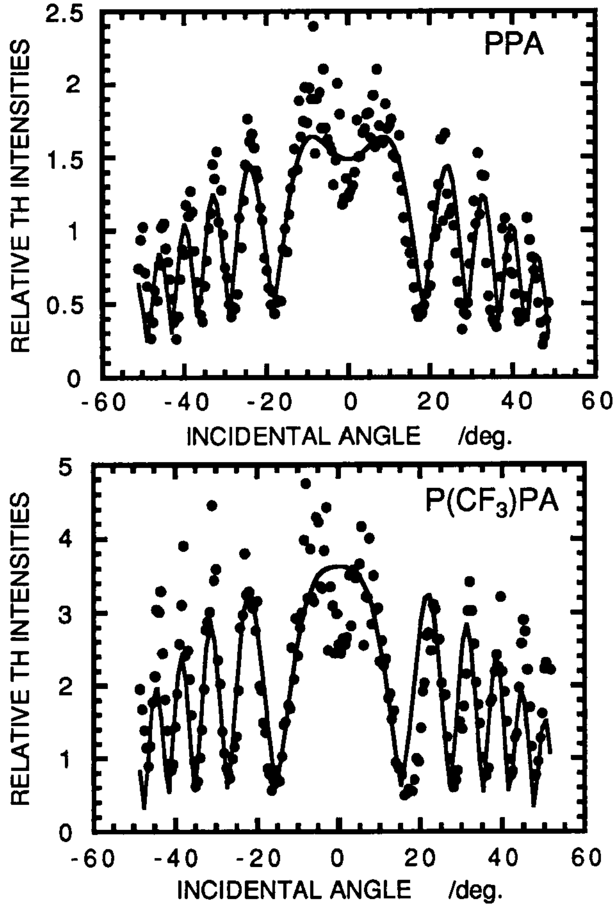

Figure 3 Typical Maker fringe patterns of PPA and $P(CF_3)PA$ thin films.

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with increasing λ_{max} of absorption in contrast with PDPAs. For example, the values of $\chi^{(3)}(\lambda_{max})$ for PPA, poly-*o*-(trifluoromethyl) phenylacetylene (P(CF$_3$)PA), poly-*o*-(tri-methylsilyl)phenylacetylene (P(Me3Si)PA) and poly-*o*-(trimethylgermyl)phenylacetylene (P(Me3Ge)PA) were determined as 5.4×10^{-13} (352 nm), 3.0×10^{-12} (439 nm), 1.7×10^{-11} (536 nm) and 2.6×10^{-11} esu (548 nm), respectively (Table 1). It should be noted that in the case of P(Me3Si)PA and P(Me3Ge)PA, THG was obtained under the weak resonant condition.

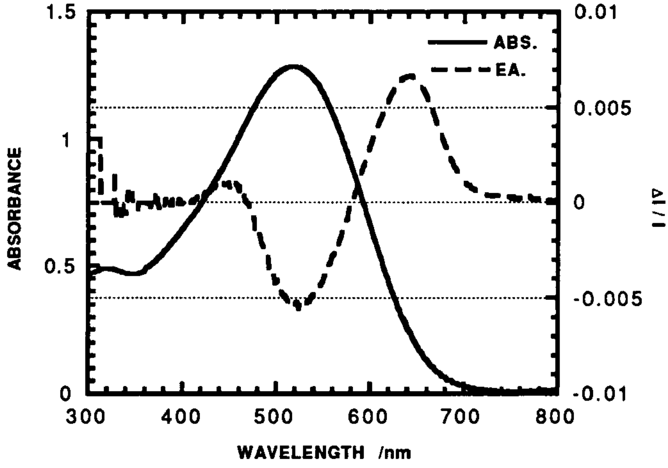

Figure 4 Absorption and electroabsorption spectra of P(Me3Ge)PA thin film.

Electroabsorption

The second-order energy derivative of the absorption spectrum indicates the main features of absorbance change (EA) spectrum, as shown in Figure 4. The change of optical absorbance $\Delta\alpha$ under an electric field leads to the change of refractive index Δn through Kramers-Kronig (K-K) transformation (Eq.(2)). Since the frequency of external electric field is low and the system can be treated as a steady state, the K-K transformation is applicable to the PPA film. It should be noted that $\Delta\alpha$ is induced by an optically linear process. The complex third-order susceptibility $\chi^{(3)}(-\omega;\omega, 0,0)$ in cgs unit can be calculated by

$$\chi^{(3)}(\omega;\omega,0,0) = \frac{n\Delta n - k\Delta k}{2\pi F^2} + i\frac{n\Delta k - k\Delta n}{2\pi F^2} \qquad (6)$$

where F is the external electric field, n and k are respectively the real and imaginary

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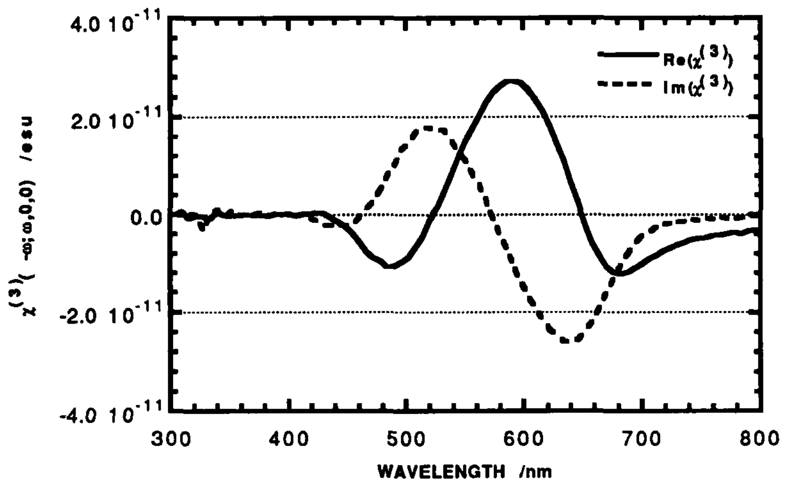

Figure 5 Dispersion of imaginary and real part of $\chi^{(3)}(-\omega;\omega,o,o)$ for P(Me3Ge)PA.

part of complex refractive index, and k=$\lambda\alpha/4\pi$. The dispersion of $\chi^{(3)}(-\omega;\omega,0,0)$ for P(Me3Ge)PA film derived from Figure 4 is shown in Figure 5. As expected, the EA spectra show the similar shape of the second derivative of the optical absorption spectra. Typical value of $\chi^{(3)}(-\omega;\omega,0,0)$ for *o*-substituted PPA was determined to be *ca.* 10^{-11}esu. Remarkable changes in the linear and nonlinear optical properties of PPAs can be achieved by varying the substituents.

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