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Optical Third-Harmonic Generation of Poly (2-Bromo-1,4-phenylenevinylene)

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Weakly electron withdrawing bromine substituted poly (2-bromo-1,4-phenylenevinylene) (PBrPV) was synthesized through water-soluble precursor method. The linear and nonlinear optical properties of PBrPV were compared with those of poly (1,4-phenylenevinylene) (PPV). The third-order nonlinear optical susceptibility, $\chi^{(3)}$, was measured by using third-harmonic generation (THG) technique at 1907 nm, fundamental wavelength. The calculated $\chi^{(3)}$ values of PPV and PBrPV were 3×10^{-12} esu and 2×10^{-12} esu, respectively.

Introduction

For realization of optical processing systems, the development of highly efficient optical nonlinear materials is expected. Some organic materials have good potential for nonlinear optical devices because of their large optical nonlinearity, very fast response time and low absorption loss as compared with inorganic semiconducting materials.¹ In particular, organic thin films which exhibit third-order optical nonlinearity have many useful applications in integrated optics such as optical bistability, optical switching and optical data processing. For these nonlinear optical materials, easy processibility such as thin-film preparation is needed for optical device application.² Among nonlinear organic materials, delocalized π -conjugated polymers are expected to possess extremely large third-order nonlinear susceptibilities.³ Recently, conducting polymers have been a special interest to many investigators because of their possibility as a nonlinear optical material.⁴ They usually possess delocalized π -conjugated systems toward their chain directions. For example, polyacetylene has been reported to show the third-order nonlinear optical susceptibility, $\chi^{(3)}$ of 1×10^{-10} esu near the resonant condition which is almost the same as the well known third-order nonlinear optical organic polymer, p-toluenesulfonate (PTS) polydiacetylene.⁵ Usually conducting polymers are in

crystalline states and they are difficult to process because of their nonfusibility and insolubility in almost all solvents. So, amorphous polymers with good processibility are expected to be good material as nonlinear optical media. Poly (p-phenylenevinylene) (PPV) is one of the examples that have been reported as amorphous optical polymers.⁶⁻⁸ High molecular weight films of PPV can be prepared from a processible precursor polymer through relatively simple reactions. PPV has been reported to show third-order nonlinear susceptibility, $\chi^{(3)}$ of 7.8×10^{-12} esu at 1.85 μm .⁹ Among the derivatized PPV structures, Kaino *et al.* investigated the poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), which has a narrower band gap compared to PPV.¹⁰ This reduction of band gap is attributed to the electron-donating character of the methoxy groups. $\chi^{(3)}$ value of PDMPV was evaluated to be 5.4×10^{-11} esu at 1.85 μm wavelength. The authors have examined the optical nonlinearity of poly(2-methoxy-1,4-phenylenevinylene) (PMPV) thin film as one of the easily processed π -conjugated polymers. The $\chi^{(3)}$ of the PMPV was revealed to be 7.9×10^{-10} esu at 602 nm by using degenerate four-wave mixing technique.^{11,12} In this paper, we report the influence of electron withdrawing substituent to third-harmonic generation. For this purpose, bromine atom as an electron acceptor was attached to the phenylene ring in PPV. Poly(2-bromo-1,4-phenylenevinylene) (PBrPV) was synthesized through water soluble precursor polymer and third-order nonlinear optical susceptibility was measured. The synthetic route and the structure of PBrPV are shown below.

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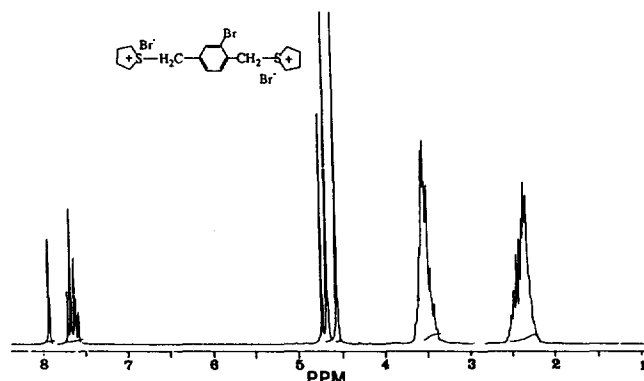
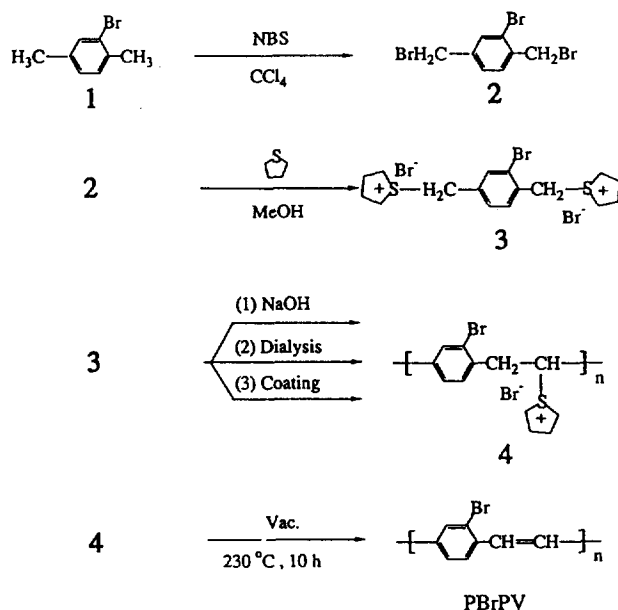


Figure 1. ^1H -NMR spectrum of 2-bromo-1,4-phenylenedimethylene bis(tetrahydrothiophenium bromide). (solvent: D_2O)



Experimental Section

Synthesis of monomer. 2-Bromo- α,α' -dibromo-p-xylene was prepared by reacting 2-bromo-p-xylene (10 g, 54 mmol) with *N*-bromosuccinimide (1.95 g, 108 mmol) in 100 ml of CCl_4 . A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90°C for 3 hrs under nitrogen atmosphere. A slightly yellow colored solution was obtained after filtration. The solution was concentrated and poured into petroleum ether. The white solid, 2-bromo- α,α' -dibromo-p-xylene, **2**, was obtained by recrystallizing the resulting precipitate from methanol. The yield was 40%. ^1H -NMR (CDCl_3): δ 7.59 (s, 1H), 7.42 (d, 1H), 7.31 (d, 1H), 4.55 (s, 2H) and 4.38 (s, 2H). The compound **2** (7 g, 20.5 mmol) and excess tetrahydrothiophene were reacted for 20 hrs at 50°C in 40 ml of methanol. The final salt monomer, 2-bromo-1,4-phenylenedimethylene bis(tetrahydrothiophenium bromide), **3**, was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration and vacuum drying. The product yield was 85% and it was very hygroscopic. ^1H -NMR (D_2O): δ 7.88 (s, 1H), 7.62 (d, 1H), 7.57 (d, 1H), 4.66 (s, 2H), 4.52 (s, 2H), 3.6-3.3 (m, 8H), 2.5-2.2

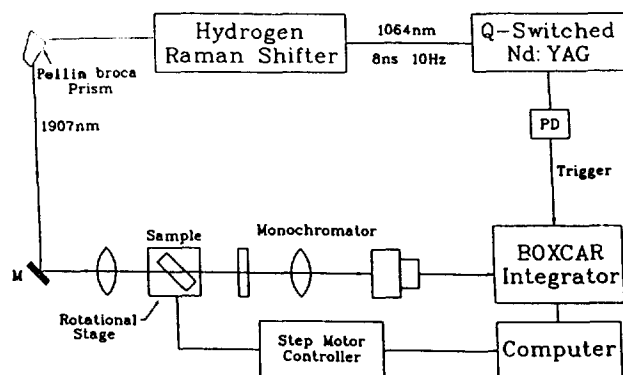


Figure 2. The schematic diagram of third-harmonic generation measurement system.

(m, 8H) and 4.7 (s, H_2O); Figure 1. The salt monomer for PPV was prepared similarly from α,α' -dichloro-p-xylene and tetrahydrothiophene following the literature method.^{6,7}

Polymerization. Synthetic method was the same as reported by us and others.^{13,14} The sulfonium salt monomer solution (1.0 M) was polymerized in an NaOH solution (1.0 M) under a nitrogen atmosphere at 0°C . A homogenous and viscous solution was obtained. The reaction was quenched by neutralization with standardized 0.5 N aqueous HCl. The precursor polymer solution was dialyzed against deionized water for 3 days using a dialysis tube with a molecular cut-off at 12000 to remove unreacted monomer and low molecular weight oligomers. Thin film was prepared by spin coating from precursor polymer solution. The solution was first filtered to remove particle impurities and then spun at 1000-2000 rpm depending on the desired thickness. Fused quartz plate was used as a reference substrate. The spin coated quartz plate was subjected to thermal elimination in vacuo (10^{-2} Torr) at 230°C for 10 hrs to transform this into the final polyconjugated polymer film.

Characterization. ^1H -NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were obtained on a Bomem Michelson series FT-IR spectrophotometer. UV-visible spectra were obtained on a Perkin-Elmer spectrophotometer. The film thickness was measured by using an Alpha step 200.

THG measurement: For third-harmonic generation (THG) measurements, Q-switched Nd:YAG laser which generates 1064 nm was used as a light source. The pulse duration and repetition rate were 8 ns and 10 Hz, respectively. To perform these measurements in transparent region where polymers have no absorption, 1064 nm was converted into 1907 nm, fundamental wavelength using a H_2 Raman shifter. The sample was mounted on the rotational stage and third harmonic intensities were measured using a PM-tube and a Boxcar integrator at each degree. Collected data were processed and maximum and minimum intensities at zero degree were obtained. The schematic diagram of the measurement system is shown in Figure 2.

Results and Discussion

FT-IR spectrum of PBrPV is compared with that of the precursor polymer film in Figure 3. The precursor polymer

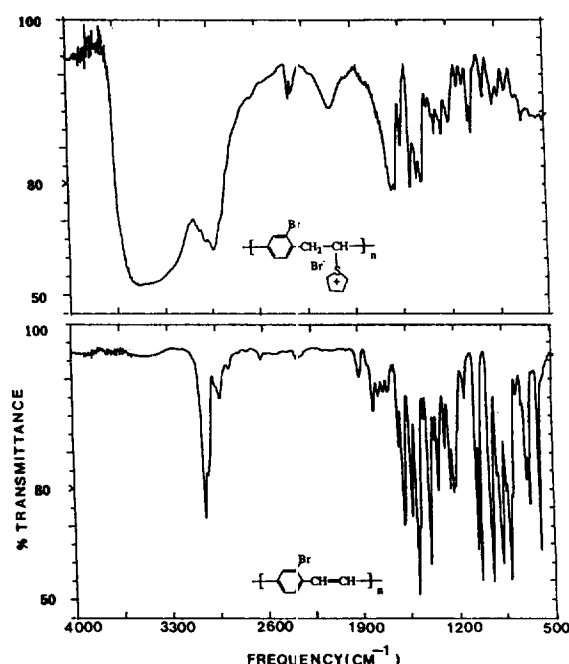


Figure 3. FT-IR spectra of (a) precursor polymer and (b) final PBrPV.

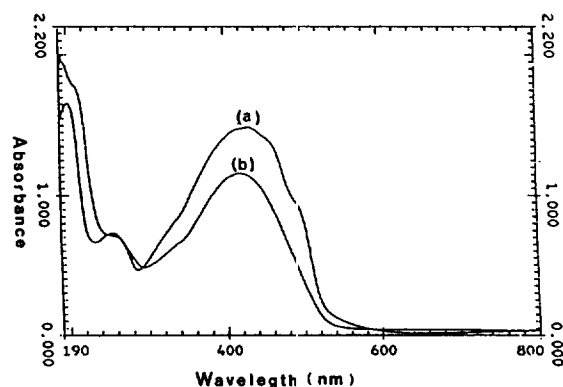


Figure 4. UV-visible spectra of polyconjugated polymers: (a) PPV and (b) PBrPV.

film exhibits a broad absorption peak at 3100-3600 cm^{-1} due to absorbed water, which disappeared in the spectrum of the eliminated film. A strong absorption peak appeared at 960 cm^{-1} after elimination, which corresponds to the out-of-plane bending mode of the trans-vinylene=C-H group. The IR spectrum of the precursor polymer also shows a small, but sharp absorption peak at the same position. This results from a premature elimination which occurred during film casting. Figure 4 shows UV-visible spectra of unsubstituted PPV and PBrPV. The maximum absorption position and the absorption edge of PBrPV (420 nm/525 nm) have moved slightly to shorter wavelength when compared with those of PPV (428 nm/530 nm). This can be explained by the hypsochromic effect of the bromine substituent. The PBrPV sample is nonabsorbing at the wavelength (636 nm) used in third-harmonic generation experiment.

Third-order nonlinear susceptibilities of polymers are determined by measuring third harmonic intensities as a function

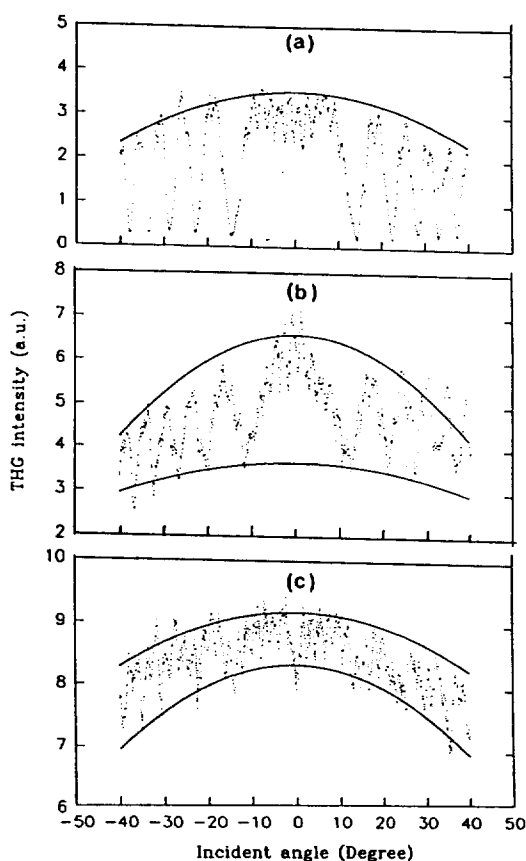


Figure 5. Maker fringe patterns of (a) fused quartz, (b) PPV and (c) PBrPV.

of incident angle between -40° and 40° . Fused quartz was used as a reference. As the polymers were coated on fused quartz, it is necessary to calibrate the interference effect between sample film and substrate quartz. The following equation is used for the calibration.^{15,16}

$$I_{\text{film}} = \frac{I_{\text{max}} + I_{\text{min}}}{2} - \frac{I_{\text{quartz}}}{2}$$

where I_{max} and I_{min} are envelopes of the superimposed THG pattern. Figure 5 shows Maker fringe patterns of the fused quartz (a), PPV (b) and PBrPV film (c) on the fused quartz substrate. These Maker fringe patterns are caused by interferences between free and bound harmonic waves and the periodicity is due to the difference of interaction length by the rotation of sample. The third-order nonlinear optical susceptibility, $\chi^{(3)}$ of the thin-film sample was calculated using the following equation.^{9,17,18}

$$\chi^{(3)} = \frac{2}{\pi} \chi_s^{(3)} \frac{\sqrt{I_{3\omega}}}{l} \left/ \frac{\sqrt{I_{3\omega,s}}}{l_{c,s}} \right.$$

where l is the sample thickness (assumed to be much thinner than the coherence length), $\chi_s^{(3)}$ and $l_{c,s}$ are the third-order nonlinear susceptibility and the coherence length of the fused quartz substrate, respectively, and $I_{3\omega}$ and $I_{3\omega,s}$ are the measured peak intensity values in the fringe patterns of the thin-films and fused quartz. The measured film thicknesses of PPV and PBrPV are 0.11 μm and 0.23 μm , respectively. $\chi^{(3)}$ value and coherence length of reference quartz (1 mm

thickness) are 2.76×10^{-14} esu and $18.41 \mu\text{m}$.^{15,19} The calculated $\chi^{(3)}$ values of PPV and PBrPV were 3×10^{-12} esu and 2×10^{-12} esu, respectively. It is well known that $\chi^{(3)}$ value is in inverse proportion to the band gap energy of nonlinear optical media.²⁰ According to UV-visible spectra in Figure 4, the band gap energy of PBrPV is slightly larger than that of PPV. It is well consistent with the measured $\chi^{(3)}$ values. Conclusively, the introduction of electron-withdrawing bromine atom to PPV is reported to be effective in increasing the band gap due to the decrease in the π -conjugation length, and thus the $\chi^{(3)}$ value of PBrPV film is slightly decreased.

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Single-phase Gallium Nitride on Sapphire with buffering AlN layer by Laser-induced CVD

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The laser-assisted chemical vapor deposition (LCVD) is described, by which the growth of single-phase GaN epitaxy is achieved at lower temperatures. Trimethylgallium (TMG) and ammonia are used as source gases to deposit the epitaxial films of GaN under the irradiation of ArF excimer laser (193 nm). The as-grown deposits are obtained on c-face sapphire surface near 700°C, which is substantially reduced, relative to the temperatures in conventional thermolytic processes. To overcome the lattice mismatch between c-face sapphire and GaN ad-layer, aluminum nitride (AlN) is predeposited as buffer layer prior to the deposition of GaN. The gas phase interaction is monitored by means of quadrupole mass analyzer (QMA). The stoichiometric deposition is ascertained by X-ray photoelectron spectroscopy (XPS). The GaN deposits thus obtained are characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and van der Pauw method.

Introduction

Gallium nitride (GaN) is one of the most promising semiconductors for optoelectronic devices, which can be used in

the region of blue light emission. It has a direct band gap energy of 3.39 eV.¹ Recently, the electrical and optical properties as well as the crystalline quality of epitaxial GaN film have been improved by introducing a thin buffer layer of