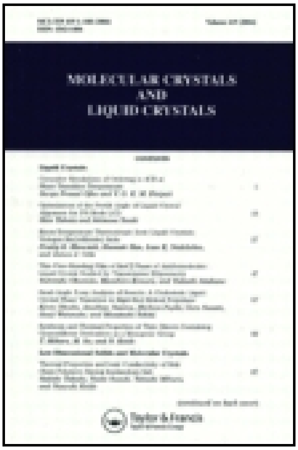

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Optical Third-Harmonic Generation of Poly(1,4-Phenylenevinylene) Derivatives Containing Stilbene Moiety

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OPTICAL THIRD-HARMONIC GENERATION OF POLY(1,4-PHENYLENE VINYLENE) DERIVATIVES CONTAINING STILBENE MOIETY

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Abstract PPV derivatives containing electron-donating and electron-withdrawing group attached stilbene moiety, poly[2-methoxy-5-(2-phenylethenyl)-1,4-phenylenevinylene] (PMPEPV), poly[2-(2-phenyl ethenyl)-1,4-phenylenevinylene] (PPEPV), poly[2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylenevinylene] (PCEMPV) and poly[2-(2-(4-trifluoromethyl)phenyl)ethenyl-1,4-phenylenevinylene] (PFEMPV) were synthesized through a water-soluble precursor polymers, and their third-order nonlinear optical susceptibilities were determined by using third-harmonic generation measurement technique at 1907 nm, fundamental wavelength. The measured $\chi^{(3)}$ values of PMPEPV, PPEPV, PCEMPV and PFEMPV were 2.1×10^{-12}, 1.7×10^{-12}, 1.2×10^{-12} esu and 0.9×10^{-12} esu, respectively.

INTRODUCTION

Nonlinear optics is expected to play a major role in the technology of photonics. Photonics is emerging as a multidiciplinary new frontier of science and technology.[1] For realization of optical processing systems, the development of highly efficient nonlinear optical 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. 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.[2,3]

Among nonlinear organic materials, delocalized π-conjugated polymers have been a special interest to many investigators because of their possibility as a nonlinear optical material.[4,5] They usually possess delocalized π-conjugated systems toward their chain directions.

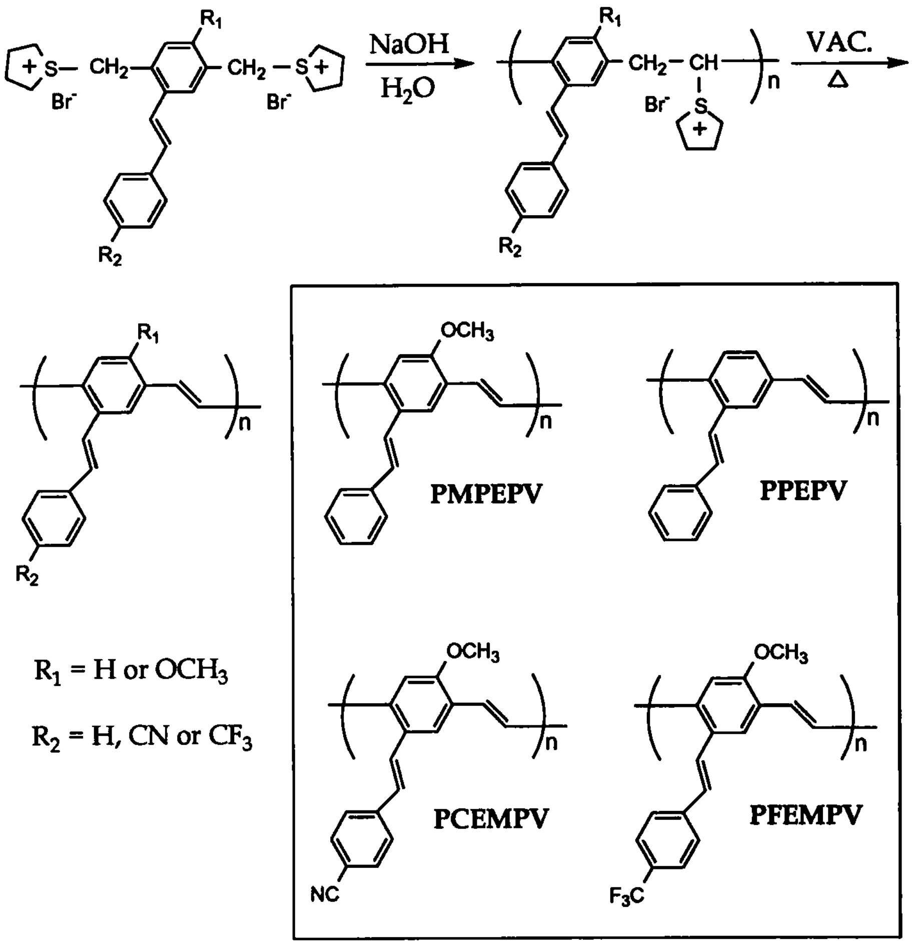
Conducting polymers are usually in crystalline states and they are difficult to process because of their nonfusibility and insolubility in almost all solvents. So, amorphous polymers with good processibility are expected to be good materials as nonlinear optical media. Poly(p-phenylenevinylene) (PPV) is one of the examples that have been reported as amorphous polymers. PPV has been reported to show third-order nonlinear optical susceptibility, $\chi^{(3)}$, of 7.8 x 10^{-12} esu at 1.85 μm.[6] Among the substituted PPV derivatives, Kaino et al. investigated the poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), which has a narrower band gap compared to PPV. The $\chi^{(3)}$ value of PDMPV was evaluated to be 5.4 x 10^{-11} esu at 1.85 μm wavelength.[7]

Here, we report the influence of substituents to optical third-harmonic generation. We synthesized PPV derivatives containing electron-donating and electron-withdrawing group attached stilbene moiety. Poly[2-methoxy-5-(2-phenylethenyl)-1,4-phenylene vinylene] (PMPEPV), poly[2-(2-phenylethenyl)-1,4-phenylenevinylene] (PPEPV), poly[2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylenevinylene] (PCEMPV) and poly[2-(2-(4-trifluoromethyl)phenyl)ethenyl-1,4-phenylenevinylene] (PFEMPV) were synthesized through a water-soluble precursor route and their third-order nonlinear optical susceptibilities were determined by using third-harmonic generation measurement technique at 1907 nm, fundamental wavelength. The polymer structures and synthetic schemes are shown below.

EXPERIMENTAL SECTION

The salt monomers for PMPEPV[8], PPEPV[8], PCEMPV[9] and PFEMPV[10] were prepared similarly from following the literature methods. The salt monomers were dissolved in deionized water and the monomer solutions were polymerized in 0.5 N NaOH solution at 0 °C. After polymerization, homogeneous and viscous solutions were obtained. The reaction was quenched by neutralization with 0.5 N aqueous HCl solution, and the nuetralized polyelectrolyte presursor solution were dialyzed against deionized water for 7 days to remove unreacted monomers and low molecular weight oligomers using a dialysis tube with a molecular weight cutoff at 12 000. The spin-coated precursor polymer films were subjected to thermal elimination in vacuo (10^{-2} torr) at 210 °C for 3 h to transform them into the final polyconjugated polymer films.

Synthetic Scheme



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. For the 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 a 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.

RESULTS AND DISCUSSION

Figure 1 shows the UV-visible spectra of a) PMPEPV, b) PPEPV, c) PCEMPV and d) PFEMPV, respectively. All of the polymers showed distinct two absorption bands. The absorption maxima of about 330 nm are due to the π-π^* transitions of trans stilbene moieties in polymer chain, and the another absorption bands about 420 nm are due to the π-π^* transitions of the conjugated main chain double bonds. As shown in Figure 1, the position of maximum absorption and absorption intensities which are due to the π-π^* transition of trans stilbene moieties of the four kinds of polymers are the same. But the maximum absorption intensities around at 420 nm due to the π-π^* transition of the conjugated vinylene double bonds strongly depend upon the substituents.

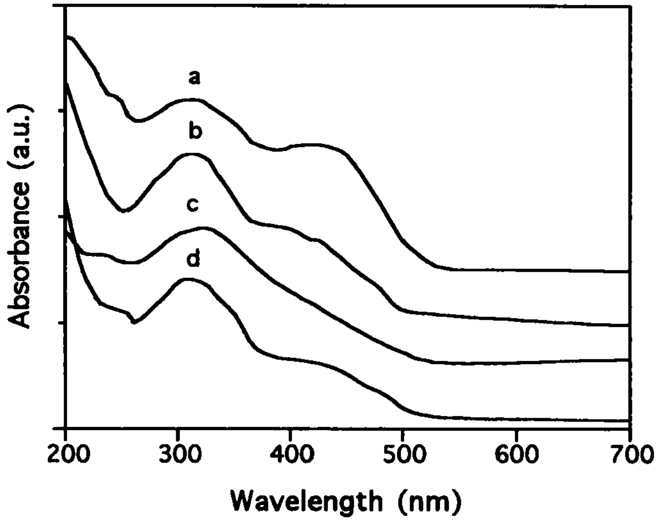


Figure 1 UV-visible spectra of a) PMPEPV, b) PPEPV c) PCEMPV and d) PFEMPV

The stronger the electron-withdrawing power of the substituents, the worse the electron delocalization through the polymer backbone, so the absorption intensities are gradually diminished. All of the polymers are non-absorbing at the 636 nm used in third-harmonic generation experiment. Third-order nonlinear optical susceptibilities of polymers are determined by measuring third harmonic intensities as a function of incident angle between -40° and 40°. Fused quartz was used as a reference. The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of the thin-film samples were calculated using the following equation.[11,12]

$$\chi^{(3)} = \frac{2}{\pi}\,\chi_s^{(3)}\,\frac{(I_{3\omega})^{1/2}}{\ell} \Big/ \frac{(I_{3\omega,s})^{1/2}}{\ell_{c,s}}$$

where ℓ is the sample thickness (assumed to be much thinner than the coherence length), $\chi^{(3)}_s$ and $\ell_{c,s}$ are the third-order nonlinear susceptibility and the coherence length of the fused quartz substrate, respectively, and I_{3w} and $I_{3w,s}$ are the measured peak intensity vaules in the fringe patterns of the thin films and fused quartz. The $\chi^{(3)}$ value and coherence length of reference quartz (1.0 mm thickness) are 2.76 x 10^{-14} esu and 18.41 μm.[11] The measured $\chi^{(3)}$ values of PMPEPV, PPEPV, PCEMPV and PFEMPV were 2.1 x 10^{-12}, 1.7 x 10^{-12}, 1.2 x 10^{-12} esu and 0.9 x 10^{-12} esu, respectively. The $\chi^{(3)}$ values are decreased with increasing the electron-withdrawing power of the side chains. All the measured $\chi^{(3)}$ values of our polymers are slightly smaller than that of PPV. It is explained that the packing ability of the polymer chains and coplanality between phenylene ring and vinylene units might be broken down because of the bulky side stilbene moieties, although the conjugation lengthes of our polymers are more extended than that of PPV by introduction of the stilbene moieties. Especially, the strong electron-withdrawing nitrile or trifluoromethyl groups decrease the π-electron density and also disturb the delocalization of the π-electrons in the conjugated polymer chains. So $\chi^{(3)}$ values of the polymers which have strong electron-withdrawing groups such as PCEMPV and PFEMPV are quite low. On the basis of structural change of the polymers, all of the above observations are consistent with our conclusions.

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