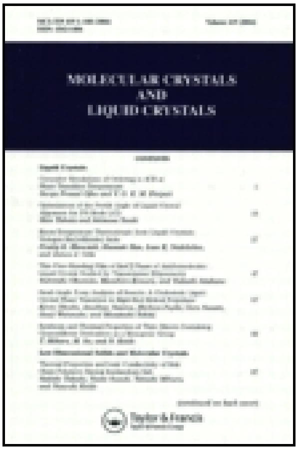

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Jeong-Ik Lee, Do-Hoon Hwang, Hong-Ku Shim, Minyung Lee, Sung-Kyu Yu & Geon Joon Lee (1994): Optical Third Harmonic Generation of Poly(2-Alkoxy-1,4-Phenylenevinylene)'S, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 247:1, 121-128

To link to this article: http://dx.doi.org/10.1080/10587259408039197

Mol. Cryst. Liq. Cryst. 1994, Vol. 247, pp. 121–128
Reprints available directly from the publisher

Printed in the United States of America

OPTICAL THIRD HARMONIC GENERATION OF POLY(2-ALKOXY-1,4-PHENYLENEVINYLENE)'S

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Abstract A series of poly (2-alkoxy-1,4-phenylenevinylene)'s was synthesized by water-soluble precursor method. In this paper, three poly(1,4-phenylenevinylene) (PPV) derivatives were included, poly (2-methoxy-1,4-phenylenevinylene), poly(2-butoxy-1,4-phenylenevinylene) and poly (2-dodecyloxy-1,4-phenylenevinylene). These polymers were characterized using UV-visible, FT-IR spectroscopy and DSC, TGA thermal analyzer. The third order nonlinear optical susceptibilities of the polymers were determined using third harmonic generation (THG) method at 1907 nm, fundamental wavelength. Measured $\chi^{(3)}$ values are 10^{-11} ~ 10^{-12} esu order and as the side chain length is increased, the $\chi^{(3)}$ value is decreased because of the side chain effect on conjugation and of volume fraction.

Keywords : Poly(1,4-phenylenevinylene) (PPV) , Poly(2-alkoxy-1,4-phenylenevinylene) , Third Harmonic Generation (THG) , Side chain length

INTRODUCTION

Recently, as the laser technology is developed, the research about nonlinear optical phenomena which come out from intense laser beam is greatly progressed.[1] Nonlinear optics is applicable to many areas of present and future information and image processing technologies, such as optical information storage, frequency mixers, light modulators, optical switches and optical logic.[2]

Especially, studies on organic materials as potential candidates for applications in optical devices have been greatly investigated because of their large optical nonlinearity, very fast response time and low absorption loss as compared with inorganic materials.[2] Among organic nonlinear optical materials, conjugated polymers

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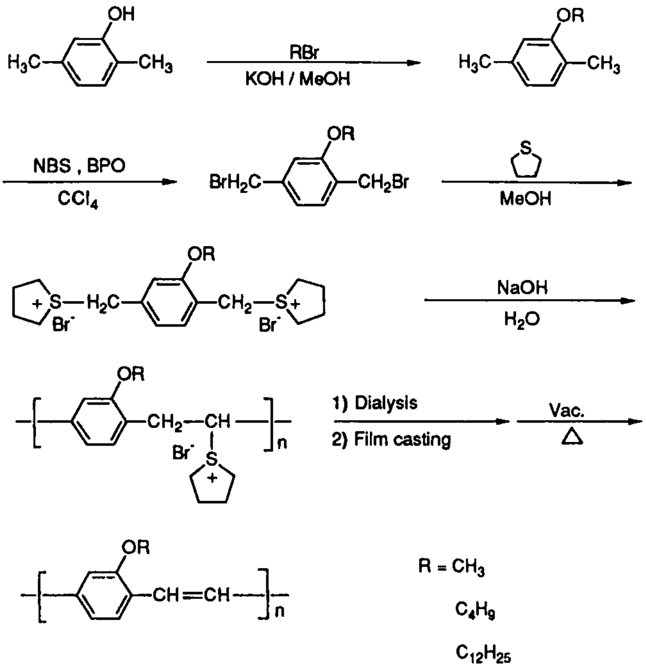
with extensive π-electrons delocalization have emerged as an important class of third order nonlinear optical materials because of the large π-electrons contribution to optical nonlinearity.[3] Phthalocyanine, polyacetylene and polydiacetylene have high $\chi^{(3)}$ values of 10^{-10} esu.[4] But these organic materials have difficulty in processing because of their nonfusibility and insolubility. So processible polymers are expected for application. Poly(1,4-phenylenevinylene) (PPV) can be prepared through processible process and have large $\chi^{(3)}$ value of 7.8×10^{-12} esu which is determined by third harmonic generation (THG) technique at 1.85 μm.[5] It is well known that as the band gap of polymer is decreased, the $\chi^{(3)}$ value is increased.[4] So electron-donating group substituted-PPV's have higher $\chi^{(3)}$ values than that of PPV.[6]

In this paper, we report some results of the third harmonic generation measurements on thin films of poly(2-methoxy-1,4-phenylenevinylene) (PMPV), poly(2-butoxy-1,4-phenylenevinylene) (PBPV) and poly(2-dodecyloxy-1,4-phenylenevinylene) (PDPV) which are electron-donating alkoxy group substituted-PPV's. We attached various alkoxy groups on the phenylene ring of PPV to investigate the side chain effect on $\chi^{(3)}$ value, and determined $\chi^{(3)}$ values by comparison third harmonic intensities with that of fused quartz. Polymers were systhesized through water-soluble precursor method[7, 8], and synthetic route and structures of these polymers are shown below.

Scheme

Syntheses of Polymers



EXPERIMENTAL

Monomer synthesis

Alkoxy-p-xylenes were prepared by reacting the 2,5-dimethylphenol with alkylbromide. But methoxy-p-xylene was prepared from commercially available compound. By reacting of alkoxy-p-xylenes with N-bromosuccinimide (NBS) in CCl_4, bisbromomethyl compounds were obtained. The sulfonium salt monomers, 2-alkoxy-1,4-phenylene dimethylene bis(tetrahydrothiophenium bromide) were obtained by reacting bisbromomethyl compounds with excess tetrahydrothiophene for 20 hours at 50℃ in methanol. Pure salt monomers were obtained by concentration of the reaction solutions, precipitation in cold acetone, filtration, and drying under reduced pressure. The products were white powder and very hygroscopic.

Polymerization

Solutions (1.0 M) of sulfonium salt monomers were polymerized in NaOH solution (1.0 M) under nitrogen atmosphere at 0℃. When yellowish gel-like materials were formed, small amount of methanol was added to solvate those materials and polymerizations were quenched by neutralization with 0.5 N aqueous HCl. The precursor polymer solutions were dialyzed for 3 days using dialysis tube (Sigma) with a molecular cut-off at 12,000. The polymer solutions were filtered and then coated on fused quartz plate using spin coater. The coated precursor polymer films were subjected to thermal treatment in vacuum at 210℃ for 10 hours to transform into the final polyconjugated polymer films.

Characterization

^{1}H-NMR spectra of salt monomers were recorded on a Brucker AM 200 spectrometer. FT-IR spectra of polymers were obtained with Bomem Michelson series FT-IR spectrophotometer. UV-VIS-NIR spectra were measured by Shimadzu UV-3100S. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) were performed under nitrogen gas (N_2) atmosphere at a heating rate of 10℃/min with Dupont 9900 analyzer. Thicknesses of spin-coated polymer films were measured by using an Alpha step 200.

$\chi^{(3)}$ measurement

Third harmonic generation technique was performed to determine $\chi^{(3)}$ values of polymers. 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. 1064 nm was converted to 1907 nm using H_2 Raman cell to perform this measurement in transparent region which corresponds to the nonresonant region of three-photon resonance. The film sample was mounted on a rotational stage and rotated around an axis perpendicular to the laser beam polarization. Third harmonic intensities were measured using PM-tube and Boxcar integrator. Schematic diagram of measurement system is shown in figure 1.

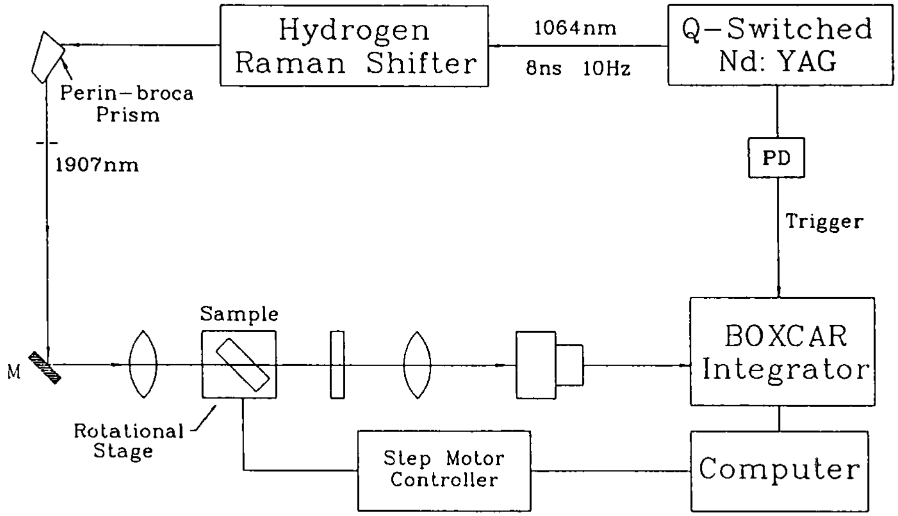


FIGURE 1 Schematic diagram of third harmonic measurement system.

RESULTS AND DISCUSSION

The ^{1}H-NMR spectra of the salt monomers well agree with the anticipated data. In DSC analyses of precursor polymers, two endotherm peaks were appeared. The lower temperature endotherm peak at 100℃ corresponds to the loss of absorbed water during film casting and the higher temperature one between 170℃ and 200℃ to the elimination reaction of HCl and tetrahydrothiophene. TGA thermograms indicated that these polymers are stable until 400℃.

The precursor polymer film exhibits a broad absorption at 3100-3600 cm^{-1} due to absorbed water, which disappeared in the spectrum of the final polyconjugated polymer. A strong absorption peak appears at 960 cm^{-1} after elimination, indicating that the vinylene C=C bonds formed have the trans configuration. 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 reaction that occurred during film casting.

Figure 2 shows UV-VIS-NIR spectra of fully eliminated PMPV, PBPV and PDPV. There are no aborptions at 600-2000nm. This indicates that these polymer films are nonresonant at 636 nm wavelength used in third harmonic generation experiment. The broad, long wavelength absoptions with maxima around 350-500 nm are due to π-π^* transitions of the polyconjugated systems. The maxima of the longest-wavelength absorptions for π-π^* transitions were found to be 450 nm for PMPV, 440nm for PBPV and 400 nm for PDPV, respectively. As the chain length of alkoxy group increases, the position of maximum absorption gradually shifts to the shorter wavelength region. This indicates the shortening of conjugation length is due to the rotational motion of phenyl ring caused by longer alkoxy side chain.

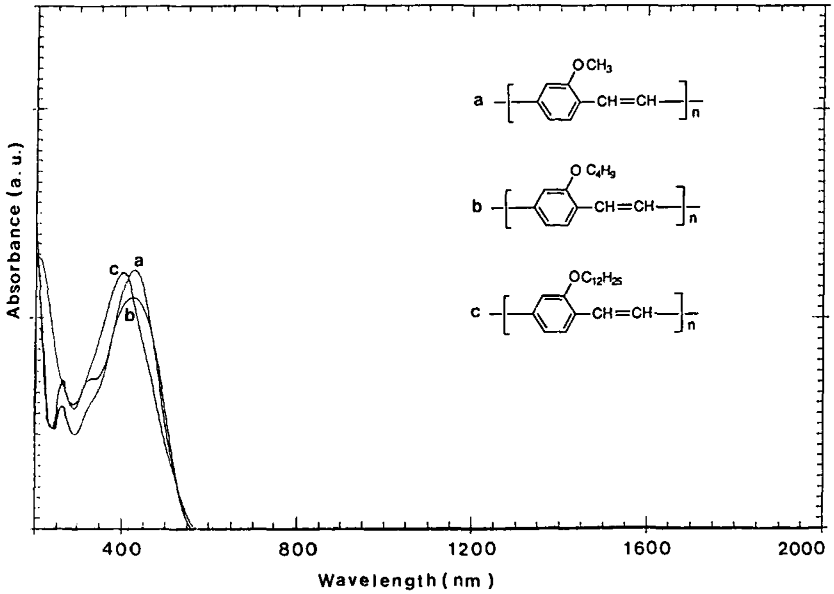


FIGURE 2 UV-VIS-NIR spectra of the conjugated polymers.

To determine the third order nonlinear optical susceptibilities of polymers, the third harmonic intensities of polymers and fused quartz were measured in function of the angle of incidence. As the polymers were coated on fused quartz, it is necessary to calibrate the interference effect between film and substrate.[6, 9]

$$I_{film} = (I_{max} + I_{min})/2 - I_{quartz}/2$$

To obtain I_{max} and I_{min}, maximum and minimum points of zero degree, Maker-fringe patterns were curve fitted. Figure 3 shows curve fitted Maker-fringe patterns of the polymers and fused quartz substrate. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, of the thin film sample (much thinner than the coherence length) was calculated using the following equation.[5, 6, 9, 10]

$$\chi^{(3)} = \frac{2}{\pi}\,\chi^{(3)}_{s}\left(\frac{I_{3w}^{1/2}}{l}\right)\left(\frac{l_{c,s}}{I_{3w,s}^{1/2}}\right)$$

where l is the sample thickness, $\chi^{(3)}_{s}$ and $l_{c,s}$ are the third order nonlinear susceptibility and the coherence length of the fused quartz, respectively, and I_{3w} and $I_{3w,s}$ are the third harmonic intensities of film and reference fused quartz. Measured $\chi^{(3)}$

values and film thicknesses are shown in table I. These data show that as the alkoxy side chain length is increased, the $\chi^{(3)}$ value is decreased.

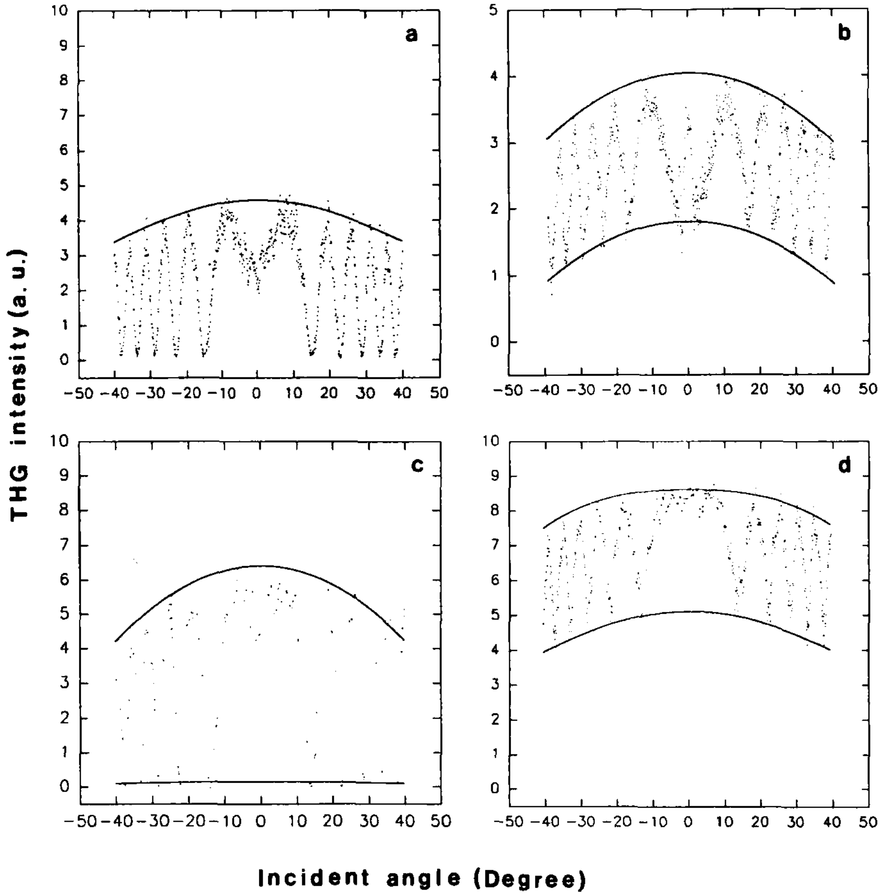


FIGURE 3 Maker fringe patterns of (a) fused quartz, (b) PMPV, (c) PBPV and (d) PDPV.

This result is explained by following two reasons. One is band gap energy difference of polymers. It is well known that $\chi^{(3)}$ value is in inversely propotional to band gap energy.[4] From UV-VIS-NIR spectra, we know that the band gap energy is increased with increasing of the alkoxy side chain length. The other is the effect of NLO chromophore density. As the side chain length is increased, the NLO chromophore density is decreased because of the increased volume fraction.

TABLE I Band gap energies and third order nonlinear coefficients, $\chi^{(3)}$.

	PMPV	PBPV	PDPV
I_{3w}	1.80	0.92	4.58
Thickness (μm)	0.017	0.025	0.132
Band gap energy (eV)	2.25	2.31	2.33
$\chi^{(3)}$ (10^{-12} esu)	11.94	5.81	2.45

* $\chi^{(3)}_{s} = 2.76\times10^{-14}$ esu $I_{3w,s} = 4.57$ $l_{c,s} = 18.41\ \mu m$[11]

CONCLUSION

The PMPV, PBPV and PDPV were synthesized to investigate alkoxy-substituent effect on the $\chi^{(3)}$ value. According to UV-VIS-NIR spectra of polymers, as the side chain lengh is increased, the λ_{max} is blue shifted. $\chi^{(3)}$ is measured by THG technique, and the trend of decreasing $\chi^{(3)}$ value with increasing of the side chain length reflects the contribution of the increase of band gap energy and volume fraction.

ACKNOWLEDGEMENT

J. I. Lee wishes to express his thanks to J. B. Choi for his measurement of thickness.

REFERENCES

1. G. R. Meredith, B. Buchalter and C. Hanziik, J. Chem. Phys., 78, 1533, (1983).
2. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
3. G. M. Carter, M. K. Thakur, Y. J. Chen and J. V. Hryniewicz, Appl. Phys. Lett., 47, 457, (1985).
4. C. Sauteret, J-P. Herman, R. Fray, F. Pradere, J. Ducuing, R. H. Baughman and R. R. Chance, Phys. Rev. Lett., 36, 956, (1976).
5. T. Kaino, K-I. Kubodera, S. Tomaru, T. Kurihara, S. Saito, T. Tsutsui and S. Tokito, Electronics Letter, 23, 1095, (1987).
6. K-I. Kubodera, Nonlinear Optics, 1, 71, (1991).
7. H-K Shim, D-H Hwang and K-S Lee, Makromol. Chem., 194, 1115, (1993).
8. H-K Shim, S-W Kang and D-H Hwang, Bull. Korean Chem. Soc., 14(1), 43, (1993).
9. F. Kajzar, J. Messier and C. Rosilio, J. Appl. Phys., 60, 3040, (1988).

10. S. Tomaru, K. Kubodera, S. Zembutsu, K. Takeda and M. Hasegawa, Electronics Letters, 23, 595, (1987).
11. B. Buchalter and G. R. Meredith, Applied Optics, 21, 3221, (1982).