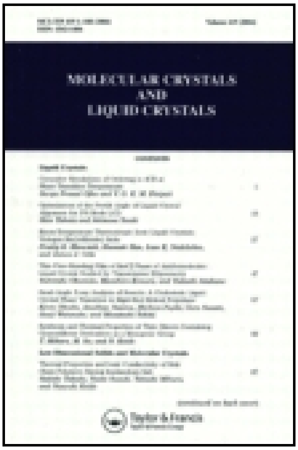

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THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF ONE-DIMENSIONAL CONJUGATED POLYMERS

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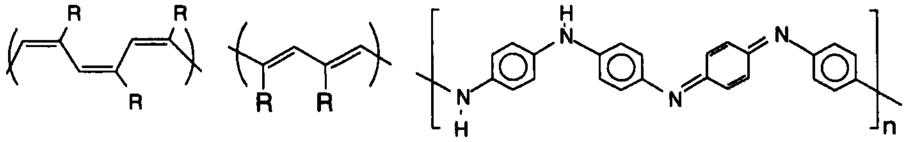
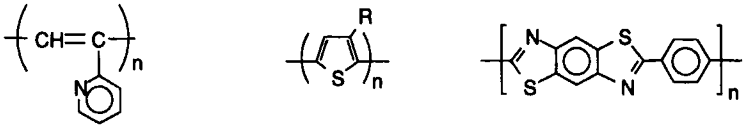
Abstract We have measured third-harmonic susceptibilities in various one-dimensional conjugated polymer films at a fundamental wavelength of 1.907 μm. The relationship between polymer structure and the third-order nonlinear optical responses of four kinds of processable conjugated polymer systems were studied: substituted polyacetylenes, polyaniline, polythiophene derivatives and poly(*p*-phenylene benzothiazole). We discuss the influence of planarity and conformation on the effective conjugation and also demonstrated the alignment of polymer chain by stretching and flow orientation to obtain the enhanced third-order nonlinear optical susceptibility.

INTRODUCTION

Conjugated π-electrons exhibit various unique opto-electronic responses. One of the simplest conjugated systems is a one-dimensional conjugated polymer polyacetylene. Besides metallic conductive property with doping, nonlinear optical responses of polyacetylene attracted a lot of attentions. Large values of third-order nonlinear optical susceptibilities and their frequency dispersion have been reported by several research groups.[1] Although polyacetylene has these interesting properties, it exhibits poor stability and processability. There have been various efforts to improve the physical properties of polyacetylene. Among them substituted polyacetylenes recently open the new research field for various applications.[2] There were pioneer works on third-order nonlinear optical properties on substituted polyacetylenes.[3] After development of new catalyst systems, a lot of acetylenes substituted with bulky substituents can be polymerized to give high molecular weight compounds.[2] In this paper we overview the third-order nonlinear optical properties of one-dimensional conjugated polymers such as substituted polyacetylenes, polyaniline, polythiophene derivatives and poly(*p*-phenylene benzothiazole) (PBT) in terms of the polymer structure and third-harmonic (TH) optical susceptibilities.



substituted polyacetylene polyaniline



poly(pyridylacetylene) polythiophene PBT

FIGURE 1 One-dimensional conjugated polymers used in this study.

POLYACETYLENE AND SUBSTITUTED POLYACETYLENES

The third-harmonic susceptibilities $\chi^{(3)}{}_{1111}$ (-3 ω; ω, ω, ω) of fully oriented crystalline *trans*-polyacetylene were obtained to be 9 x 10^{-9} and 1.7 x 10^{-8} esu at fundamental wavelengths of 1.064 and 1.907 μm, respectively.[1] Although the measurement conditions, that is, fundamental wavelengths and band gaps of materials are different, these values are exceptionally high. For the practical application, especially waveguide applications, materials should meet several physical property requirements. We apply substituted polyacetylenes to processable third-order nonlinear optical materials. As mentioned before, we should carefully compare the properties of materials under the same condition. However we discuss the material performance of various one-dimensional conjugated polymers based on the third-harmonic susceptibility ($\chi^{(3)}$) at a fundamental wavelength of 1.907 μm, because we obtained the good correlation between $\chi^{(3)}$ value at 1.907 μm and a dispersion of third-order nonlinear optical response determined by electroabsorption measurement.[4]

Tabata et al. developed Rh complex catalyst systems which stereoregularly polymerize various substituted acetylenes.[5] The polyphenylacetylene polymerized by Rh catalyst has a *cis*-rich structure in comparison with W catalyst. The absorption edge was blue-shifted and the $\chi^{(3)}$ value is small in the order of 10^{-13} esu as shown in Figure 2 and Table 1. Theoretical prediction suggests that the third-order nonlinear optical response of polyene is sensitive to their conformation. Therefore structure-property relationship should be studied in well-defined conformers of polyene. By conversion from *cis* to *trans* isomer of polyphenylacetylene, the $\chi^{(3)}$ value increased by factor of 1.5.

In the case of polyacetylenes substituted with a fused ring, a λmax of absorption shifted to longer wavelengths and $\chi^{(3)}$ values increased with an increase of a ring size as shown in Figure 2 and Table 1. The copolymer with α-naphthylacetylene and 9-anthrylacetylene is one of the good candidate for processable one-dimensional conjugated polymers.

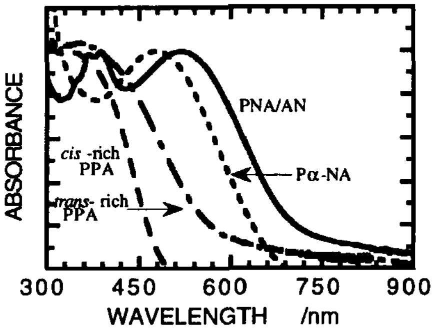
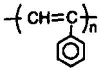
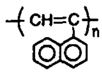
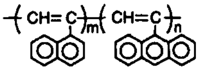


FIGURE 2 Absorption spectra of thin films for polyacetylene substituted with a fused ring.

TABLE 1 Third-order nonlinear susceptibilities of substituted polyacetylenes.

Polymer		*$\chi^{(3)}$ (-3ω;ω,ω,ω) ($\times 10^{-12}$ esu)	
PPA		(*cis*-rich)	0.36
		(*trans*-rich)	0.54
Pα-NA			12
PNA/AN			40

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

MODULATION OF CONJUGATED MAIN CHAINS

The electronic state of one-dimensional conjugated polymers can be modified by various ways. One is a direct modification of conjugated main-chain. For example, upon protonation of the emeraldine base of polyaniline through treatment with an HCl, dramatic change of absorption was observed.[6] The formation of a half-filled polaron state affects the nonlinear optical responses as shown in Figure 3. The other is an indirect way using the intermolecular interaction of side chain groups. Poly(2-pyridylacetylene) is soluble in protonic solvents, allowing conjugation to be controlled by protonation of its pyridine rings.[7] ^{13}C NMR study indicated that the poly(2-pyridylacetylene) doped with HCl has a high content of *cis* geometry in the main chain. The HCl molecules may play two roles as a dopant and a linkage between pyridine rings which increases π-electron delocalization along the main chain. The HCl linkage between pyridine rings red-shifts the absorption edge and enhances $\chi^{(3)}$ as summarized in Table 2. Depending on the nature of substituent groups, additional functions of substituted polyacetylene are induced which can not be expected in pristine polyacetylene.

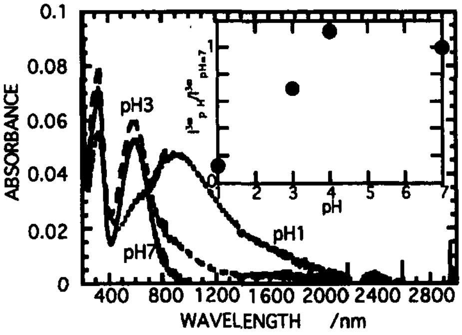
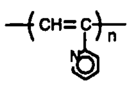
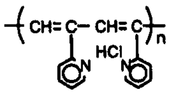


FIGURE 3 Optical absorption spectra and third-harmonic intensities of polyaniline films upon protonation.

TABLE 2 Third-order nonlinear susceptibilities of poly(2-pyridylacetylene)s.

polymer		$^*\chi^{(3)}$ (-3ω;ω,ω,ω) (x10^{-12} esu)
P2PyA		**0.15**
P2Py(HCl)A		**0.57**

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

ALIGNMENT AND PACKING OF POLYMER CHAINS

In one-dimensional conjugated polymers, there is only one dominant tensor component γ_{xxxx} of the third-order nonlinear optical susceptibility which is located along the polymer backbone. In the case of the amorphous polymer films, the isotropically averaged hyperpolarizability is reduced by factor of 5. Therefore the control of orientation of polymer chain is quite important in one-dimensional conjugated polymer systems.

We applied mechanical stretch and flow orientation methods to align the conjugated polymer chain in order to highly utilize the one dominant tensor component. The third-harmonic $\chi^{(3)}$ values of stretched poly(3-dodecylthiophene) films increased with a stretching ratio (L/L_0).[8] The changes of x-ray diffraction and optical absorption suggest that the helix of the polymer chain is stretched and the effective conjugation is also extended. The torsion angle of neighbouring thiophene rings in solid-state helical structure could be reduced upon stretching as shown in Figure 4.

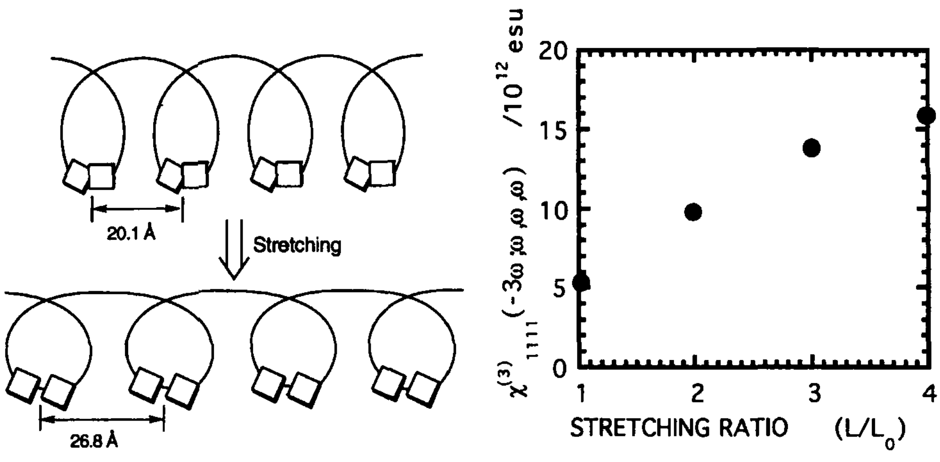


FIGURE 4 Solid-state polymer structure and third-harmonic susceptibilities of poly(3-dodecylthiophene) upon stretching.

The orientational distribution and packing of polymer chains were investigated in poly(*p*-phenylene benzobisthiazole) (PBT) Langmuir-Blodgett (LB) films.[9] The tensor components of $\chi^{(3)}$ on the PBT LB film with a surface pressure of 50 mN/m were determined to be $\chi^{(3)}{}_{1111} = (16.6 \pm 2.5) \times 10^{-12}$ and $\chi^{(3)}{}_{2222} = (2.0 \pm 0.3) \times 10^{-12}$ as shown in Figure 5. A Gaussian distribution function with a standard deviation of σ=0.40 gives a practical description of the orientational distribution of PBT polymer chains induced by a flow orientation.

Research group of KAIST developed soluble substituted polyacetylene via ring-opening metathesis reaction of 4, 4-disubstituted-1, 6-heptadiyenes.[10] Both linear optical absorption and $\chi^{(3)}$ value depend on the volume fraction of conjugated main chain in the same way.[11] Therefore we were able to estimate the $\chi^{(3)}$ value of main-chain 1,6-heptadiyene polymer assuming the same density of polyacetylenes. The extrapolated $\chi^{(3)}$ value is 1.3×10^{-10} esu (1.8×10^{22} cm^{-3}) which is smaller by two orders of magnitudes than that of polyacetylene. Therefore the effective conjugation is limited by defects of polymer chain itself.

CONCLUSION

To develop efficient one-dimensional conjugated polymers for third-order nonlinear optical applications, it is required firstly to select a suitable stereoregular substituted polyacetylene, secondly to convert the isomer from *cis* to *trans* state, and thirdly to align the polymer chain. Although the substituted polyacetylene has a reduced volume fraction of conjugated polymer chain, the additional physical property can be expected.

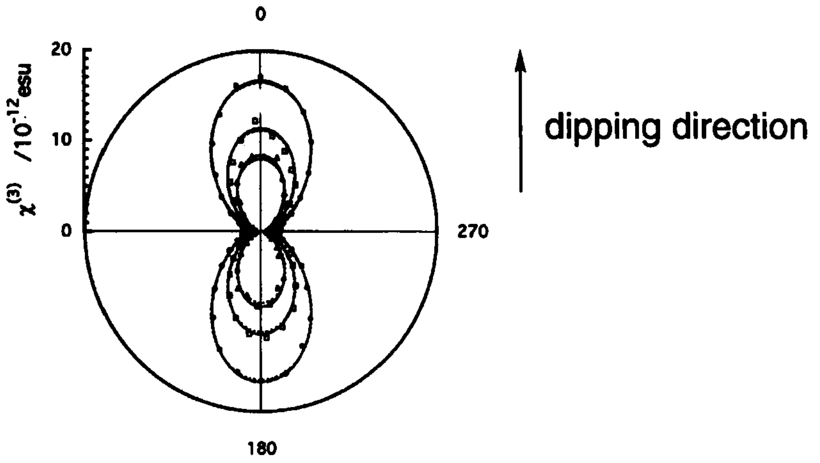


FIGURE 5 A polar plot of $\chi^{(3)}$ dependence with respect to the dipping direction PBT. The fabrication surface pressures are 30(△), 40(□), and 50 mN/m (○), respectively.

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