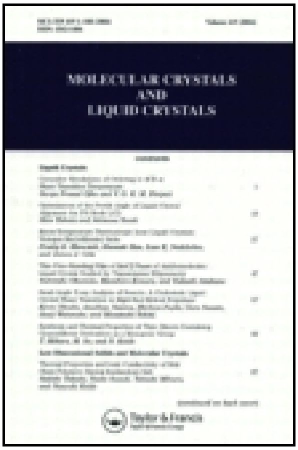

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
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Molecular Design of Conjugated Systems for Nonlinear Optics

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Molecular Design of Conjugated Systems for Nonlinear Optics

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Three types of π-conjugated systems have been developed for the third order optical nonlinearity: polythiophene and its derivatives, alkane bridged- and/or phenyl bridged-polydiynes and thermally crosslinked ones, and tetra-*tert*-butylphthalocyanines dispersed in polymethylmethacrylate. The macroscopic third order nonlinear optical susceptibility $\chi^{(3)}{}_{1111}(-3\omega;\omega,\omega,\omega)$ of the film was determined from the Maker fringes, and their application to the optical waveguide was discussed from the mode-line measurement.

INTRODUCTION

A lot of investigations have been focused on the development of nonlinear optically (NLO) active materials such as ferroelectric crystals, semiconductor-doped glasses and organic crystals. Among them organic substances are more advantageous than other materials because of the ease of molecular designs and structural control (crystal engineering), and of the processability. It is well known that the intramolecular charge transfer (CT) through π-electron conjugated systems gives large optical nonlinearities in the molecular level, whereas the centro-symmetry of the crystal structure determines the macroscopic second order nonlinearity ($\chi^{(2)}{}_{ijk}(-\omega_3;\omega_1,\omega_2)$); if the crystal is centrosymmetric, then $\chi^{(2)}$ becomes zero. Polydiacetylene (PDA) obtained by solid state polymerization was firstly reported to have large third order nonlinearity ($\chi^{(3)}{}_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$) comparable to that of semiconductors, especially parallel to the conjugated main chain.[1] In order to enhance the processability of materials can be used such techniques as polymerization,[2] molecular dispersion in guest-host systems[3] and so on.

Under these circumstances we have developed various kinds of NLO active materials based on the π-conjugation. In this paper three types of polymeric materials are discussed: the conducting polymers of polythiophene (PTh) and its derivatives, polydiynes and macrocyclic π-conjugated system (soluble phthalocyanines (Pc)) molecularly dispersed in polymethylmethacrylate (PMMA). The values of $\chi^{(3)}{}_{1111}(-3\omega;\omega,\omega,\omega)$ (abbreviated as $\chi^{(3)}$ hereafter) of these materials and their possibility to the optical waveguide application are also discussed.

POLYTHIOPHENES

Polythiophene was polymerized electrochemically as follows: The solution of thiophene monomer of 0.2 mol/l with nitrobenzene was prepared. Tetramethylammonium perchlorate (TMAP) of 0.05 mol/l was added to the solvent as a supporting electrolyte. The working electrode was an ITO glass (area of 3 cm^2). The counter electrode was a Pt plate. On polymerization, the current density of 6.7 mA/cm^2 was applied between the electrodes at the duration of 20 sec. The synthesized polymer film was washed in nitrobenzene solvent, and then perchlorate ions were extracted from the film in the solvent of nitrobenzene/TMAP. In this case the voltage of -0.8 V (vs. SCE) between reference and working electrodes was applied for 2 days. After extraction, the undoped film was washed in nitrobenzene solvent and dried up in a vacuum chamber.

On the other hand, soluble polythiophene derivatives, poly(3-alkyloxy-methylthiophene), were prepared as follows: A solution of $NaBH_4$ (5g, 0.125 mol) in 50 ml of 50% NaOH aq. was added to 3-thiophenealdehyde (28 g, 0.25 mol) in 100 ml of MeOH. The mixture was refluxed for 3 hrs and evaporated. The residue was extracted with methylenedichloride (300 ml × 3) and distilled under the reduced pressure. Yielded 3-thiophenemethanol (5.6 g, 0.05 mol) was dissolved in a mixture of 1-bromo-hexane and triethylbenzylammonium chloride in 100 ml of 50% NaOH aq., and refluxed for 5 hrs. Organic layer was washed with water, dried with Na_2SO_4 and distilled under reduced pressure. The monomer, 3-hexyloxymethylthiophene (bp. 94°C at 3 mmHg) was obtained (8.2 g, yield 84%). 2 g of the monomer was dissolved in 200 ml of MeOH which was saturated with $FeCl_3$ and refluxed for 24 hrs. Precipitated was collected by filtration and washed by Soxhlet extraction for 2 days. 1.2 g of red polymer was obtained (conversion 60%). Poly(3-dodecyloxymethylthiophene) (PDTh) has also synthesized via almost same procedure. Thickness-controlled thin films were made by spin coating of polymer solution.

From the optical absorption spectra of polythiophene derivatives, it is clearly observed that the absorption maximum shifts towards shorter wavelength by the introduction of alkyloxymethyl pendants (hyposochromic shift). This indicates the shortening of conjugation length due to the rotational motion of thiophene rings caused by longer alkyl chain. The effect of alkyl chain length on hyposochromic shift is almost negligible.

POLYDIYNES

Two types of polydiynes were prepared: one was an alkane bridged polydiyne and the other was a phenyl bridged polydiyne. The former is not a π-conjugation system, but by the interchain crosslinking due to thermal treatment it becomes a one-dimensional conjugated polymer like PDA as shown in Figure 1. In the 1-D π-conjugation systems only one tensor component of molecular optical susceptibility along the main chain γ_{xxxx} contributes dominantly to the isotropically averaged susceptibility $<\gamma>$, *i.e.*,

$$<\gamma> = (1/5)\gamma_{xxxx}.$$

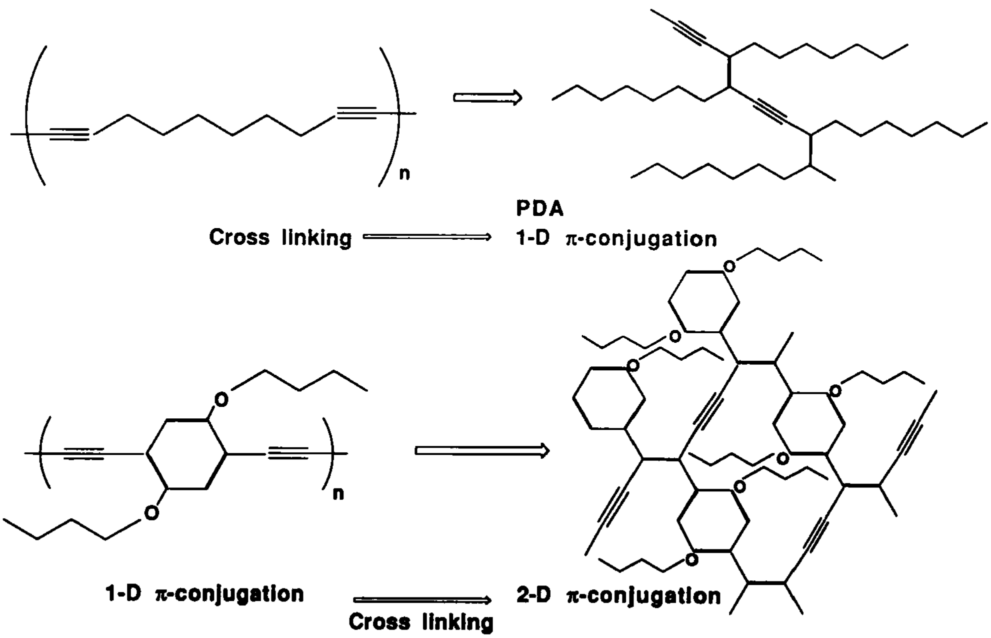
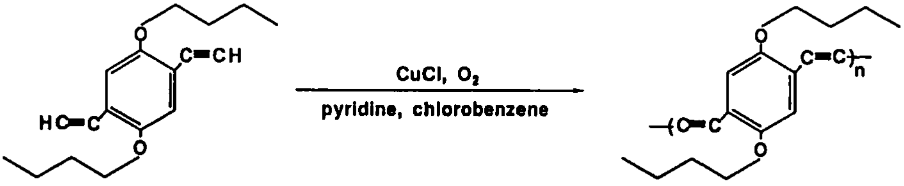


FIGURE 1 1-D and 2-D π-conjugation systems prepared by the crosslinking of alkane-bridged and phenyl-bridged polydiynes, respectively.

The latter is, on the other hand, a 1-D π-conjugation system and easily converted into the 2-D system by the interchain crosslinking. In the 2-D π-conjugation systems other tensor components also contribute to $<\gamma>$, *i.e.*,[4]

$$<\gamma> = (1/5)[\gamma_{xxxx} + \gamma_{yyyy} + (1/3)(\gamma_{xxyy} + \gamma_{xyxy} + \gamma_{xyyx} + \gamma_{yyxx} + \gamma_{yxyx} + \gamma_{yxxy})].$$

Poly(1,9-decadiyne)(PDD) is an example of alkane bridged polydiyne, and prepared as follows: 1,9-decadiyne (5 g) was dissolved in the mixed solvent of pyridine/chlorobenzene (80/20) with CuCl and N,N,N′,N′-tetramethylethylene-diamine as catalysts and polymerized under bubbling of oxygen gas at 60°C for 5 hrs. Yielded polymer was precipitated by adding methanol/HCl mixed solvent to the solution, and after filtration and washing with H_2O and acetone it was purified by the precipitation from dichloroethane/methanol solution three times. The yield was 42%. PDD was characterized with ^{1}H-NMR and optical absorption spectra. The solution of PDD and 1,2-dichloroethane was spread over the quartz substrate and then a high quality film could be obtained. Though the as prepared film was opaque, it turned to be colored, but transparent by annealing at 150°C for 48 hrs, which indicates the formation of 1-D π-conjugated system. From the IR spectra of this film the formation of C═C bonds can be confirmed. The film was applicable for the optical third harmonic generation (THG) measurement. Under the UV irra-



SCHEME 1 Polymerization of 1,9-decadiyne.

diation, however, PDD becomes dark purple in color and less applicable for THG measurement.

Poly(1,4-diethynyl-2,5-dibutoxybenzene)(PDEDBB) is an example of phenyl bridged polydiyne, and prepared by the same route as PDD (Scheme 1). Figure 2 shows ^{13}C-NMR spectra of PDEDBB in solution (a) and in the solid state (b). This result indicates that there are two different electronic states in the phenyl ring,

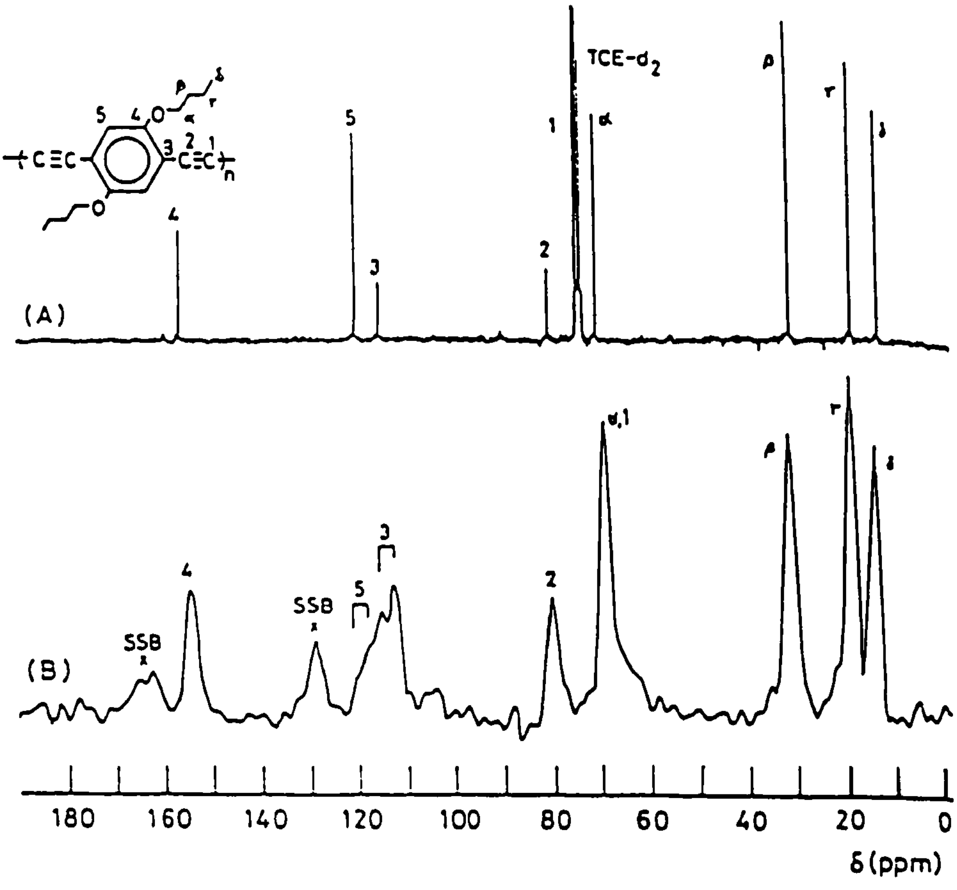


FIGURE 2 ^{13}C-NMR spectra of poly(1,4-diethynyl-2,5-dibutoxybenzene)(PDEDBB) in solution (A) and in the solid state (B).

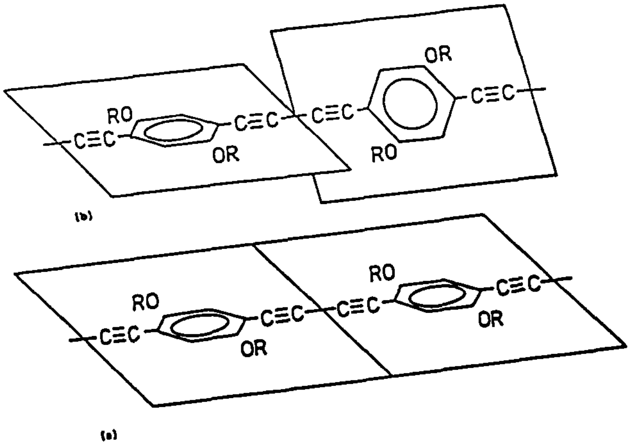
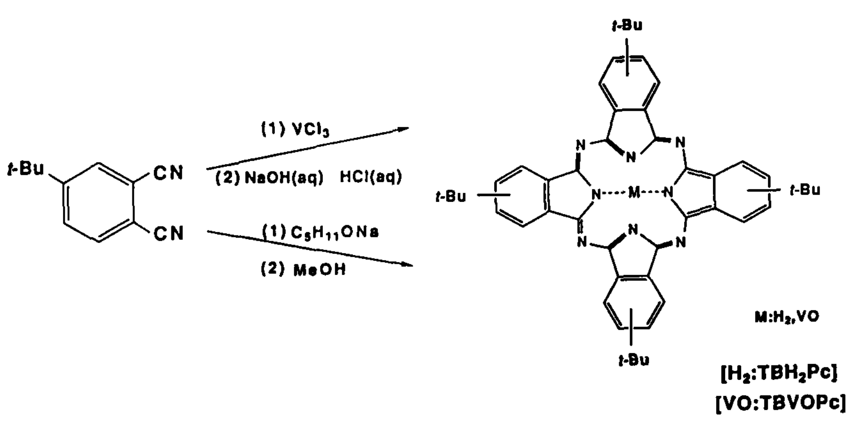


FIGURE 3 Proposed structures of PDEDBB: (a) the conjugated planar structure and (b) the non-conjugated twisted structure.

i.e., the conjugated planar structure and the non-conjugated twisted structure as illustrated in Figure 3. From the X-ray diffraction measurement it is confirmed that the cast film of PDEDBB is completely amorphous, though PDEDBB powders show some indication of crystalline diffraction.

SOLUBLE PHTHALOCYANINES

We have already reported that vanadylphthalocyanine (VOPc) has a large $\chi^{(3)}$ (ca. 10^{-10} esu at 1907 nm).[5] In order to provide an excellent solubility to polymer matrix, VOPc is modified by substituting peripheral four phenyl rings with *tert*-butyl group (TBVOPc). This compound has been synthesized according to Scheme 2. For comparison metal free tetra-*tert*-butylphthalocyanine (TBH_2Pc) has also been synthesized. The materials were thoroughly purified by column chromatography



SCHEME 2 Preparation of tetra-*tert*-butylphthalocyanines.

on silica gel using chloroform as an eluent, followed by precipitation from chloroform to methanol. Characterization was made by IR, ^{1}H-NMR, FD-MS and elemental analysis. Optically transparent films containing TBH$_2$Pc or TBVOPc in PMMA (Mn = 31,000) were obtained by spin coating of chloroform solutions onto a fused silica substrate. Refractive indices of thin films are measured by ellipsometry and mode-lines methods.

THG MEASUREMENT

Transmitted optical third harmonic generation (THG) from the thin film deposited on a fused silica substrate was observed at a wavelength of 1907 nm. The measuring system for THG is reported elsewhere.[6] The fundamental wavelength of Nd:YAG laser (1064 nm, 10 pulse/sec) was shifted by the stimulated Raman scattering in a high pressure hydrogen gas cell (30 kg/cm^2): the first Stokes radiation is 1907 nm. The incident beam is splitted into two by a beam sampler, one is used for a sample and the other for a reference. Through the monochromator, only the TH beam (636 nm) from the sample mounted on the goniometer is detected by a photomultiplier and its intensity is accumulated in the boxcar for 30 pulses at each rotational angle of the goniometer (0.5°). As a reference a fused silica can be used.

The output intensity of TH from the sample $J_{3\omega}$ is normalized at the same time with that from the reference to eliminate the fluctuation of incident light. $J_{3\omega}$ changes sinusoidally as a function of rotational angle of the plane parallel slab of sample about an axis, and appears as a set of fringes known as Maker fringes. According to Kajzar *et al*,[7] $J_{3\omega}$ is given as Equation 1,

$$J_{3\omega} = \frac{256\pi^4 J_\omega^3}{c^2} \left| \frac{A\chi^{(3)}}{\Delta\epsilon} \right|^2 \sin^2 \frac{\Delta\Phi}{2} \tag{1}$$

where J and n are respectively the light intensity and refractive index for fundamental (subscript ω) and harmonic (3ω) frequencies, $\Delta\epsilon = n_\omega^2 - n_{3\omega}^2$, A a factor arising from transmission and boundary conditions, $\Delta\Phi$ a phase mismatch ($= \Delta k l$), l the sample thickness and c is the speed of light in the free space. Under the condition of $l \ll l_c$ (coherence length), Equation 1 can be simplified as

$$J_3\omega = \frac{2304\pi^6 J_\omega^3}{c^2} \left| \frac{A\chi^{(3)}}{n_\omega + n_{3\omega}} \right|^2 \left(\frac{l}{\lambda_\omega} \right)^2 \tag{2}$$

where λ_ω is the wavelength of fundamental light.

MODE-LINES MEASUREMENT

In order to check the thin film light guide, the prism-film coupling is an essential technique. The coupling between the prism (refractive index of n_p) and the film waveguide (n_f) formed on the substrate (n_s) takes place along the bottom plane of the prism through a thin gap layer (air) of index n_c, as shown in Figure 4. The propagation constant β of the incident light beam along the waveguide film is given by

$$\beta = n_p k \sin\theta' \quad ; k = 2\pi/\lambda \tag{3}$$

where θ' is the incident angle onto the bottom of the prism, which is related to the incident angle θ outside the prism through Snell's law as

$$n_c \sin(\theta - \alpha) = n_p \sin(\theta' - \alpha) \tag{4}$$

α denotes the toe angle of the prism. If the propagation constant is in a range $n_c < \beta/k < n_f$ (guided mode), the guided wave is excited through the distributied coupling and penetrates as an evanescent wave into the film. In the waveguide film, β is expressed as

$$\beta = kn_{\text{eff}} \quad ; n_{\text{eff}} = n_f \sin\theta'' \tag{5}$$

where θ'' is the total reflection angle.

From the field equations for TE mode, the wave number in the x direction k_x can be derived in the form of *eigen value equation*,

$$k_x T = m\pi + \tan^{-1}(r_s/k_x) + \tan^{-1}(r_c/k_x) \tag{6}$$

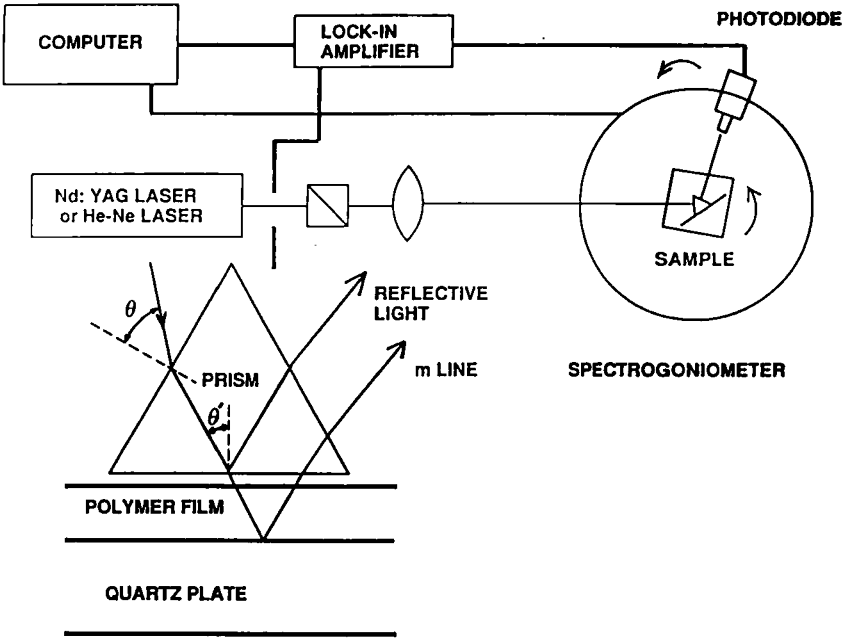


FIGURE 4 Schematic layout of Mode-line measuring system.

where $k_x = k(n_f^2 - n_{eff}^2)^{1/2}$, $r_s = k(n_{eff}^2 - n_s^2)^{1/2}$, $r_c = k(n_{eff}^2 - n_c^2)^{1/2}$, T is the thickness of the waveguide film and m = 0, 1, 2, . . . denotes the mode number. The incident beam focused on the prism base in a synchronous direction can feed the optical energy into one of the waveguide modes of the film. Since the film scatters the optical energy in the excited mode into other modes, then the beam is coupled back to the outside medium by the same prism. This phenomenon gives a series of bright lines on the screen with a bright spot on one of these lines (m-lines). From the positions and the widths of m-lines, we can determine the mode spectra, the refractive index and the film thickness. Therefore, if we can observe m-lines by means of a prism-film coupler method, this is a good evidence of guided waves. Figure 4 also indicates the schematic diagram of m-line measuring system used in this study.

RESULTS AND DISCUSSION

THG: Maker Fringes

Soluble conducting polymers, *i.e.*, PDTh, PDD and PDEDBB, were spin-coated on the fused silica substrate. The films were quite homogeneous in thickness of *ca.* 1.5 μm. Figures 5–8 show typical patterns of the incident angle dependences of TH intensities for a fused silica substrate, PDTh, PDD and PDEDBB films on

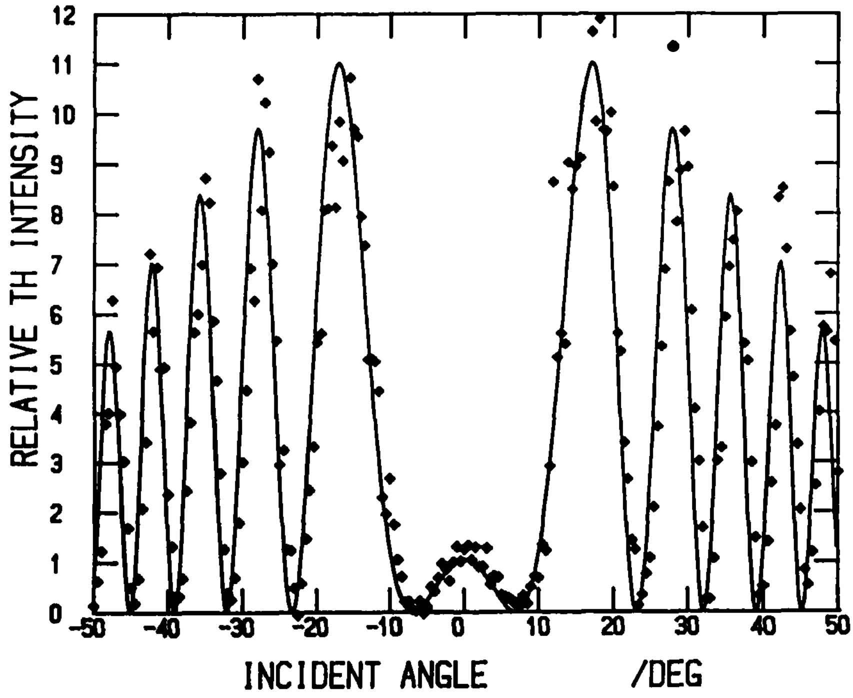


FIGURE 5 Maker fringe pattern of third harmonic (TH) intensity for a fused silica substrate. Solid line is calculated from Equation 1.

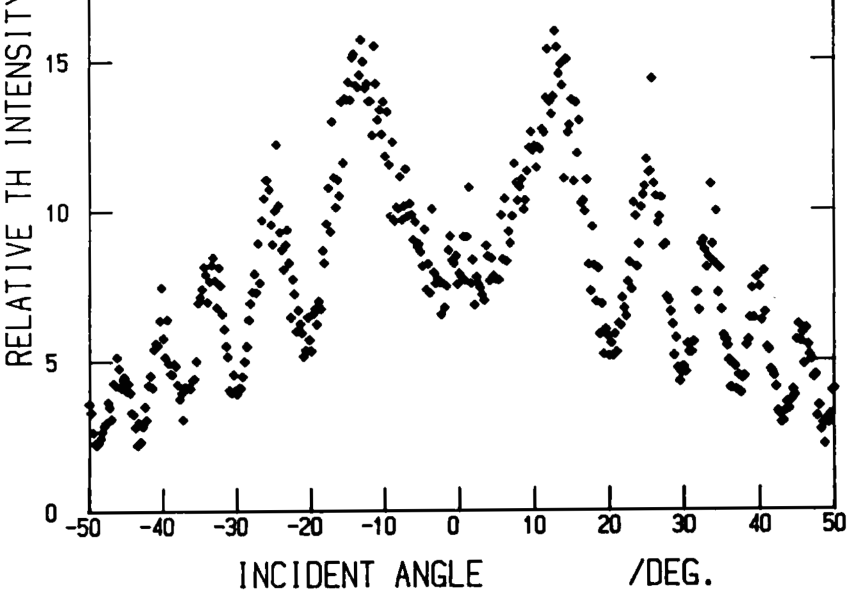
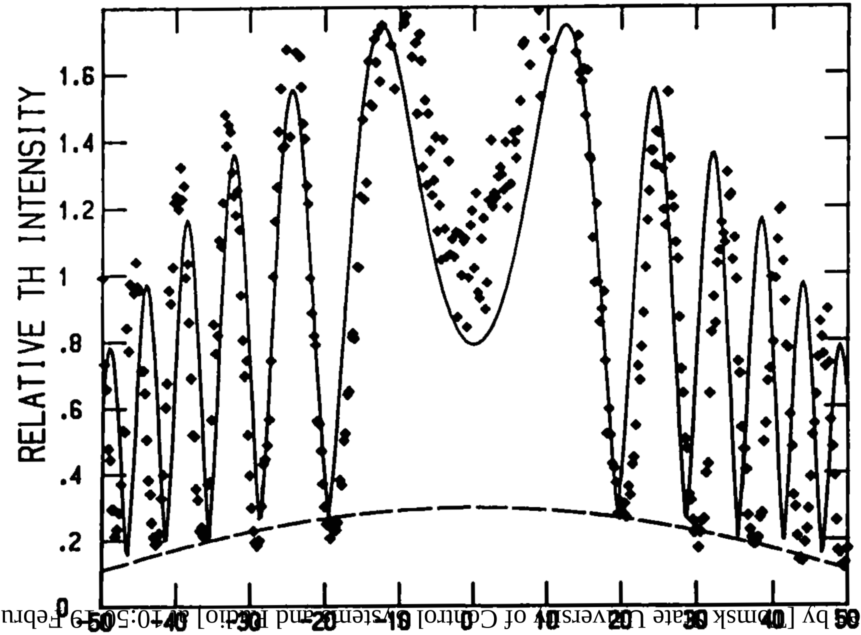


FIGURE 6 Maker fringe pattern for poly(3-dodecyloxymethylthiophene)(PDTh).



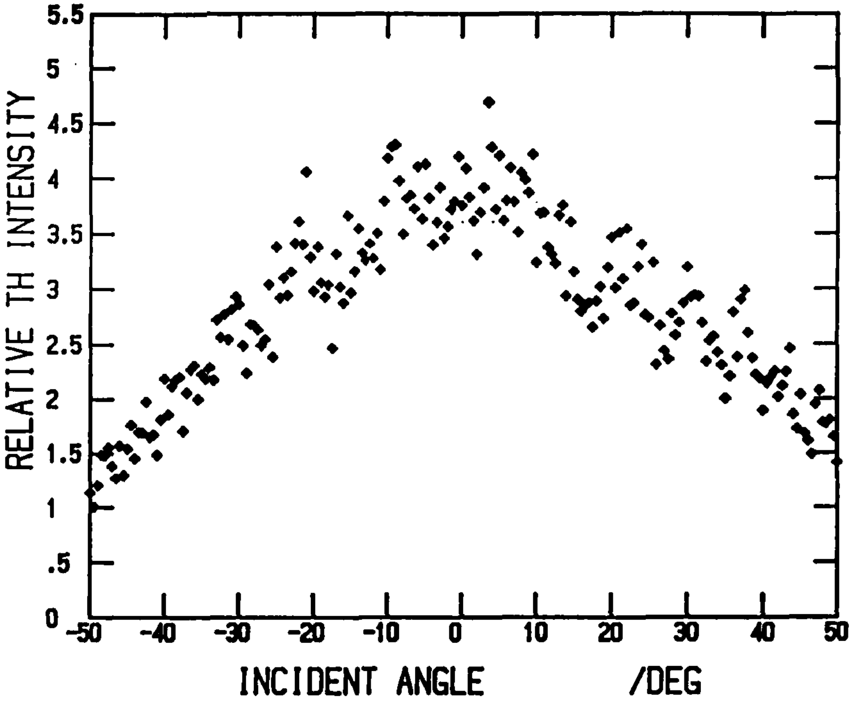


FIGURE 8 Maker fringe pattern for PDEDBB.

fused silica substrate, respectively. In the case of fused silica, the TH intensity changes sinusoidally as a function of incident angle, and coincides well with the calculated curve of Equation 1. This oscillating pattern indicates the consecutive variation of optical pathlength equal to one, two, or more coherence length l_c, respectively. The minimum points are zero except the normal incident (angle = 0), which indicates the quality of substrate being quite good. From the periodicity l_c can be estimated as 18.3 μm. This value is in good agreement with the reported value by Meredith *et al.*[8]

On the contrary, PDTh and PDD films on a fused silica substrate show the TH intensity being superposed of two components; one is a sinusoidally oscillating component and the other is an envelope of minimum points of the first component. The former is exactly the same as the fused silica substrate. The latter is due to the film itself, and its intensity follows Equation 2. In the calculation it is necessary to know the refractive indicies of the film at the fundamental (1907 nm) and TH (635 nm) wavelengths, respectively. We measured n_ω from the m-line at 1064 nm and $n_{3\omega}$ from the ellipsometry at 632.8 nm for each sample. These values are slightly changed to get a best fitting of Equation 1 to observed data points. The values of $\chi^{(3)}$ for PDTh and PDD are estimated as 5×10^{-12} and 1×10^{-13} esu respectively by using that of fused silica (2.8×10^{-14} esu).[8] In the case of crosslinked PDD the $\chi^{(3)}$ value increases about one order of magnitude (10^{-12} esu). As shown in Figure 8, the contribution from a fused silica substrate is masked due to large $\chi^{(3)}$

value of PEDBBD (1×10^{-11} esu), that is, only the component corresponding to Equation 2 appears. This is the similar result as obtained for undoped polythiophene ($\chi^{(3)} = 3.52 \times 10^{-10}$ esu).[9] These results confirm that the formation of 1-D π-conjugation enhances the third order optical nonlinearity.

Figure 9 shows the concentration dependence of $\chi^{(3)}$ in TBH_2Pc/PMMA and TBVOPc/PMMA systems. It should be noted that both phthalocyanine derivatives are quite soluble into PMMA and processable to the smooth film by means of spin coating method. The values of $\chi^{(3)}$ of TBH_2Pc and TBVOPc are respectively 3.0×10^{-12} and 7.5×10^{-12} esu, and smaller than those of unsubstituted phthalocyanines (6.0×10^{-12} esu for H_2Pc and 1.85×10^{-10} esu for VOPc). In the case of VOPc's a large difference in $\chi^{(3)}$ may come from the stacking of Pc molecules, because VOPc film has an absorption peak in the longer wavelength region than Q-band (800–850 nm) which is unobservable in TBVOPc film. This consideration is reasonable from the fact that the Q-band intensity around 830 nm in VOPc increases with thermal annealing at 125°C due to increasing intermolecular interaction. The difference in $\chi^{(3)}$ values of TBH_2Pc and TBVOPc indicates that the metal-to-ligand and/or ligand-to-metal charge transfer states introduced by metal

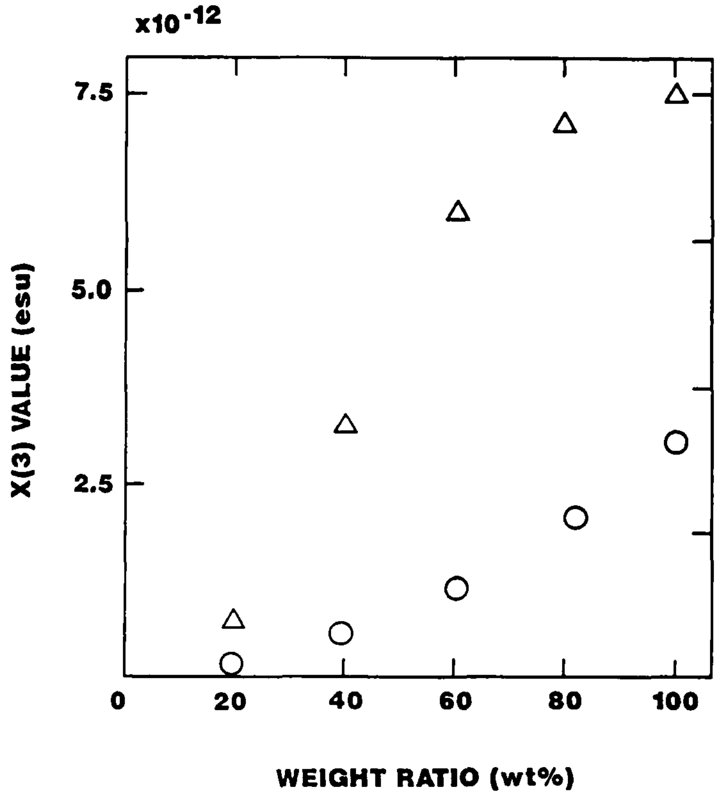


FIGURE 9 Relation between weight ratio of tetra-*tert*-butylphthalocyanines in PMMA and $\chi^{(3)}$ value: for TBH_2Pc (○) and for TBVOPc (△).

substitution contribute to the enhancement of third order susceptibility as discussed by Shirk *et al.*[10]

Mode-Lines

The refractive indices of PDTh, heat treated PDD and TBVOPc/PMMA (38.6 wt%) films at 632.8 nm (He-Ne laser) are respectively 1.92, 1.58 and 1.78. Since those of a rutile prism and the fused silica substrate are respectively 2.874 and 1.457, it is possible to couple the incident beam (He-Ne laser) from the prism with polymer films via air gap. In the case of PDD we can clearly observe m-lines as shown in Figure 10. By rotating the prism-film coupler on the spectro-goniometer, the bright spot on a fundamental m-line (m = 0) disappears and then appears on the next line. This occurs periodically; that is, the reflected beam intensity depends on the incident angle as shown in Figure 11. From the angle of the zero reflection (dip) the refractive index of polymer film can be calculated.

The relationship between film thickness and the effective refractive index n_{eff} is given from Equation 6 for each guided mode. Figure 12 shows the calculated results for the prism-film coupler using PDD film. For the film thickness of 1.65 μm, the values of n_{eff} and hence those of incident angle can be determined. It follows that the dips in Figure 11 correspond to TE_0, TE_1 and TE_2 respectively from the higher angle side. The mode lines for PDTh and TBVOPc/PMMA films are also clearly observed. These results suggest that the m-line method is useful for the judgement of applicability of conjugated polymers and/or molecularly doped host/guest polymer systems to the optical waveguide.

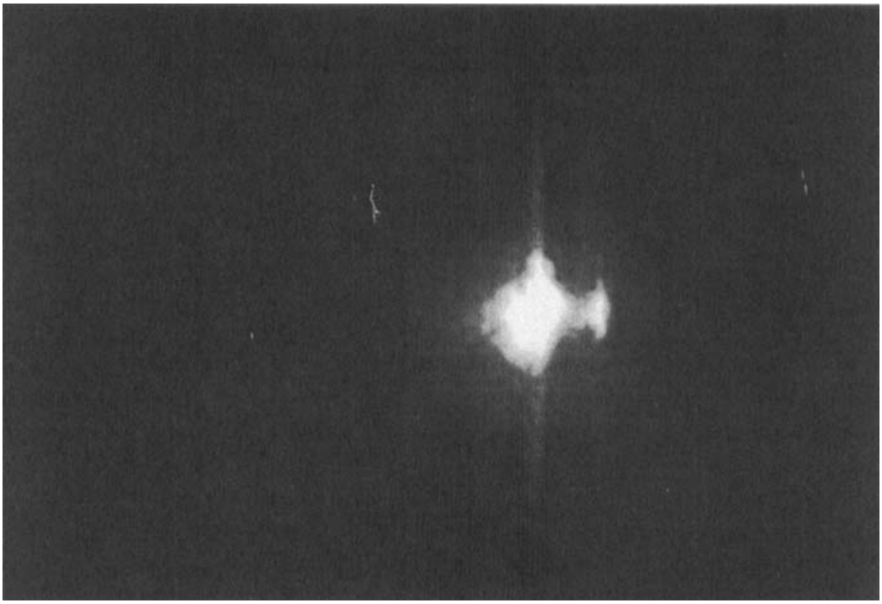


FIGURE 10 Example of mode-lines observed in PDD.

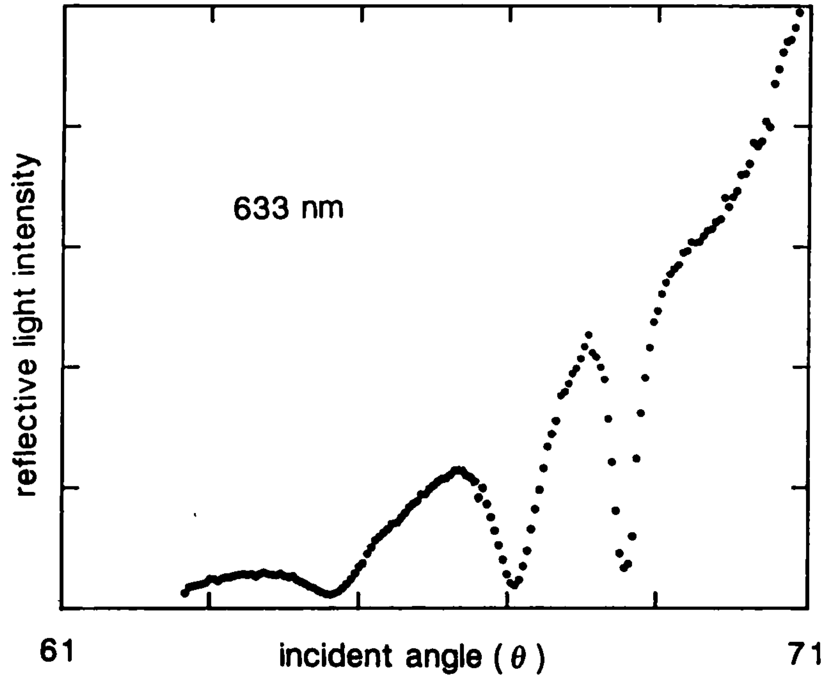


FIGURE 11 Incident angle dependence of reflected light intensity of PDD for the He-Ne laser beam.

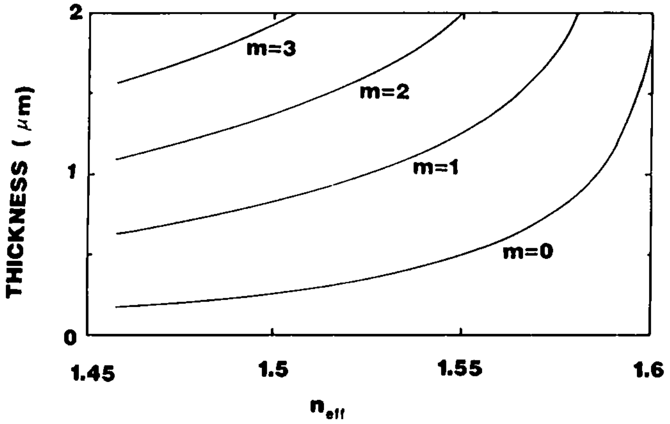


FIGURE 12 Relationship between film thickness and the effective refractive index n_{eff} calculated from Equation 6 for guided mode m = 0, 1, 2 and 3 or PDD.

CONCLUSION

It is demonstrated that one dimensional π-conjugation along the main chain of polymers such as polythiophene derivatives and crosslinked polydiynes and/or two dimensional π-conjugation of macrocyclic molecules dispersed in polymer matrices are essential approaches to the molecular design of nonlinear optically active materials. Both Maker fringe method and mode-line method are useful not only for the determination of NLO parameters but for the assessment of materials for the optical device application.

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