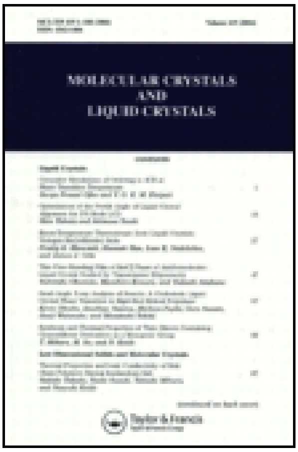

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# Molecular Design of Nonlinear Optical Polymeric Materials for Switching Device Application

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# MOLECULAR DESIGN OF NONLINEAR OPTICAL POLYMERIC MATERIALS FOR SWITCHING DEVICE APPLICATION

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Abstract Molecular design of nonlinear optical (NLO) polymeric materials for device application such as ultrafast optical switches are discussed. It is necessary to fabricate channel waveguides to realize polymeric NLO switching devices that can be driven with lower laser power. For that purposes, we have proposed a molecular structure of processable NLO polymers where the reduction of an attenuation loss and the attainments of higher processability of the polymers are achieved. Third-order nonlinear optical properties, $\chi^{(3)}$, of novel NLO polymers were around $10^{-10}$ esu at 1.5 μm wavelength region. Even in off-resonant regions, their $\chi^{(3)}$ values are around $5 \times 10^{-11}$ esu. Single mode channel waveguides of the polymers are fabricated using a standard photo-process. Attenuation loss through the film and that for the single mode waveguide at 1.32 μm wavelength was also reported.

## INTRODUCTION

Photonic devices such as ultrafast optical switches and bistable devices have attracted much attention as key elements for the future optical signal processing systems[1]. For that purpose, the development of highly efficient third-order nonlinear optical (NLO) materials are expected. Polymeric NLO materials are attractive because they exhibit ultra fast response time[2]. To realize polymeric NLO switching devices that can be driven with lower laser power, NLO materials must satisfy several requirements, such as larger optical nonlinearities, lower linear loss and higher processability as shown in Fig. 1. The optical nonlinearity for polymeric NLO materials are limited to $10^{-9}$-$10^{-10}$ esu, though, fabrication of channel waveguides is necessary for actual device application. For that purposes, the reduction of an attenuation loss and the attainment of higher processability are as much important as the enhancement of the optical nonlinearity.

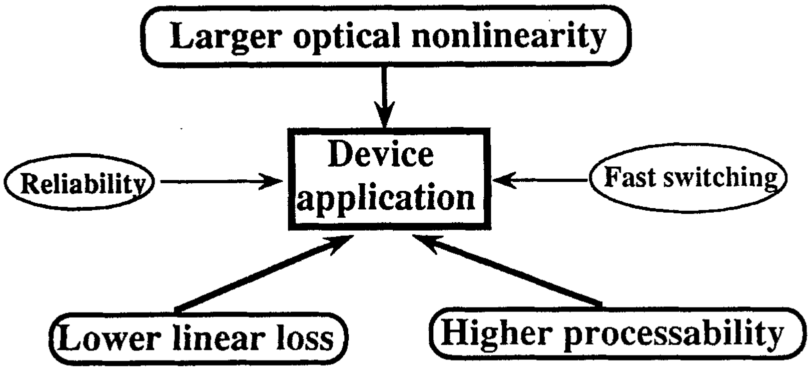


FIGURE 1 NLO material requirements for device application.

The authors have already developed novel NLO polymers with excellent processability[3]. Third-order nonlinear optical properties, $\chi^{(3)}$, of the novel NLO polymers, i.e., main-chain polymers where the nonlinearity generating dyes are actually a part of the polymer backbone, have been investigated. These main chain polymers are one possible candidate to fabricate optical waveguides with large $\chi^{(3)}$ value because the polymer can contain NLO dyes in high concentrations. There are several papers about main chain $\chi^{(3)}$ materials such as π-electron conjugation containing vinyl polymers[4] and aromatic shiff base structure based $\chi^{(3)}$ polymers[5]. We also have proposed heteroaromatic polymers as a possible material for the above mentioned purpose[6]. Figure 2 shows the molecular structure of processable NLO polymers. There seems to exist a tendency that higher $\chi^{(3)}$ polymers have a higher attenuation loss.

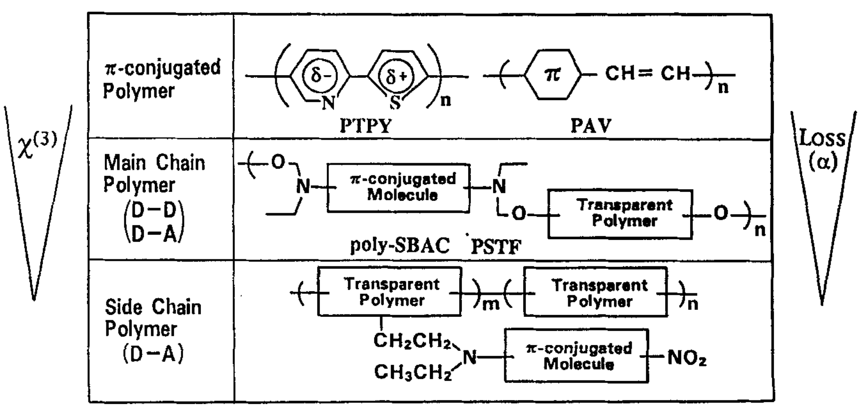


FIGURE 2 Molecular structures of processable NLO polymers.

This paper reports on NLO properties of two types of processable main-chain NLO polymers, poly-SBAC and PSTF. Single mode channel waveguide fabrication and optical propagation of the polymers are discussed.

## OPTICAL PROPERTIES OF MAIN CHAIN POLYMERS

Figure 3 shows the molecular design concept of novel main chain NLO polymers and the chemical structure of poly-SBAC and PSTF. SBAC is benzylidene aniline derivative which is symmetrically substituted by donor groups at both ends of π-conjugation. The abbreviation PSTF refers to polyurethane composed of symmetrically substituted tris-azo dye with fluorinated alkyl chains[7]. These new polymers are easy to fabricate from solution to amorphous films by conventional spin-coating or casting methods. The $\chi^{(3)}$ values have been evaluated by THG measurements using the Maker-fringe method. Experimental $\chi^{(3)}$ values of the polymer films were calculated using an equation reported earlier[8]. As a reference, silica glass with $\chi^{(3)}$ values of $2.8 \times 10^{-14}$ esu was used.

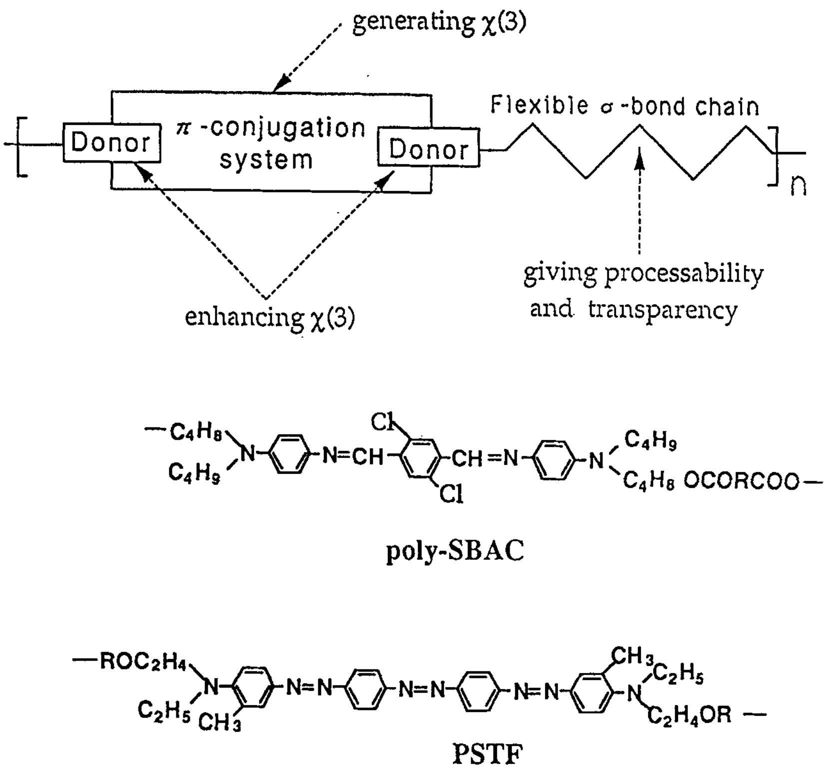


FIGURE 3 Molecular design concept of novel main-chain NLO polymers.

The $\chi^{(3)}$ wavelength dependence for a poly-SBAC thin film showed that a strong $\chi^{(3)}$ enhancement is observed when the incident wavelengths are three times the wavelengths in the absorption spectra[9]. The maximum $\chi^{(3)}$ value obtained is about $7\times10^{-11}$ esu around 1.57 μm wavelength. This $\chi^{(3)}$ can be identified as three-photon resonance.

Through a prism, a laser beam was coupled with these films and the refractive indices were estimated. Mode lines of the incident laser beam were easily detected by the prism coupling. The results (refractive index and film thickness) agree well with estimated values. We could control the refractive index of poly-SBACs by modifying the intermediate segments in the polymer.

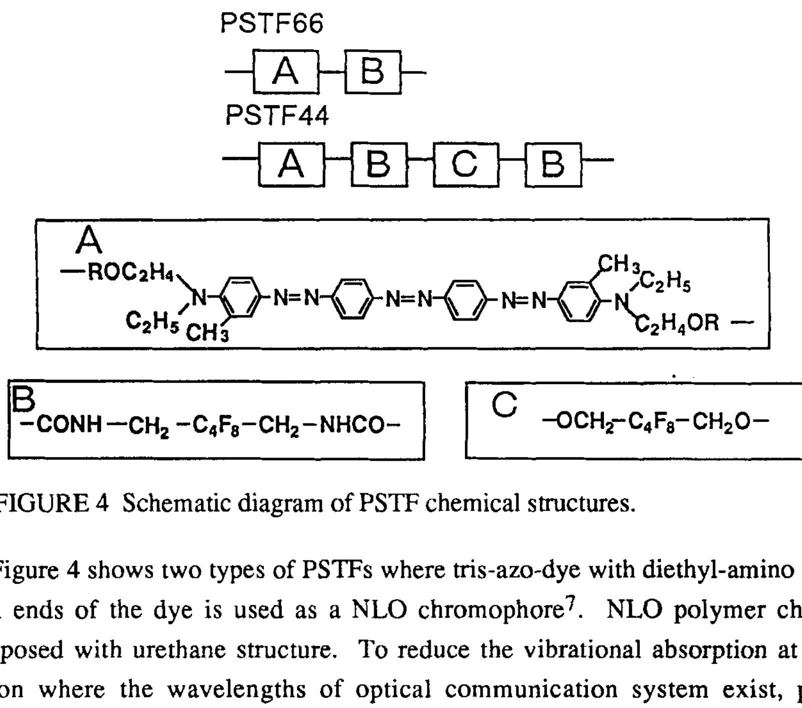


FIGURE 4 Schematic diagram of PSTF chemical structures.

Figure 4 shows two types of PSTFs where tris-azo-dye with diethyl-amino group at both ends of the dye is used as a NLO chromophore[7]. NLO polymer chain was composed with urethane structure. To reduce the vibrational absorption at near-IR region where the wavelengths of optical communication system exist, partially fluorinated alkyl-chain is used to connect the chromophore and the urethane structure. The numbers after the PSTF refer to the dye contents (in weight %) in the polymer. Absorptional maxima of the polymer is located at around 520 nm. Linear and nonlinear optical properties depend on the content of the dye in the polymer. Third-order optical nonlinearity was measured at the wavelength between 1.5 to 2.1 μm. The value was larger than $10^{-11}$ esu in the resonant and non-resonant region. Figure 4 shows the absorptional spectra and the $\chi^{(3)}$ wavelength dependence for PSTF 44. $\chi^{(3)}$ value at a resonant wavelength region is about $4\times10^{-11}$ esu. Even in a non-resonant region, the value is around $2\times10^{-11}$ esu.

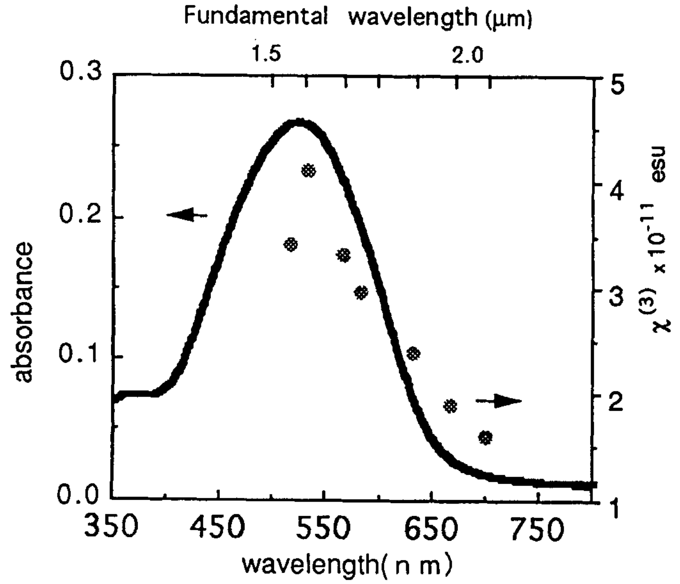


FIGURE 5 Absorption specters and the $\chi(3)$ wavelength dependence for PSTF-44

Figure 6 shows the relationship between dye contents and the refractive index of the polymer at 1.3 μm wavelength. Prism coupling method was used to measure the refractive index for the polymer thin film. The refractive index could be controlled by the dye content. The dye content for the single mode channel waveguides was decided using the result.

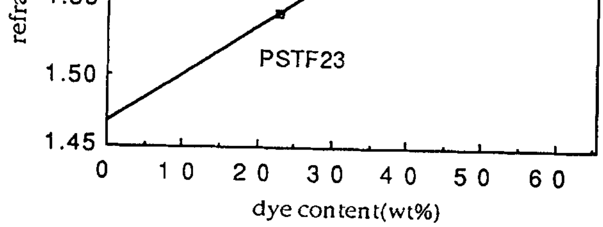


FIGURE 6 Relationship between dye contents and the refractive index of the PSTF at 1.3 μm

## WAVEGUIDE FABRICATION OF MAIN CHAIN POLYMERS

Optical transmission of the polymer is measured using a film fabricated on silica glass substrate. Attenuation loss through the film was measured by detecting the scattering loss from the films. For poly-SBAC slab waveguides, the loss values at 1.3 μm wavelength were around 2 dB/cm although those at 0.633 μm were larger than 20 dB/cm. So, poly-SBACs are promising for device applications in the Near-IR region. Channel waveguides of the polymer thin film can be obtained using a photo-bleaching technique. A refractive index difference of up to 0.005 is attained by irradiating the film with UV light through a photo mask.

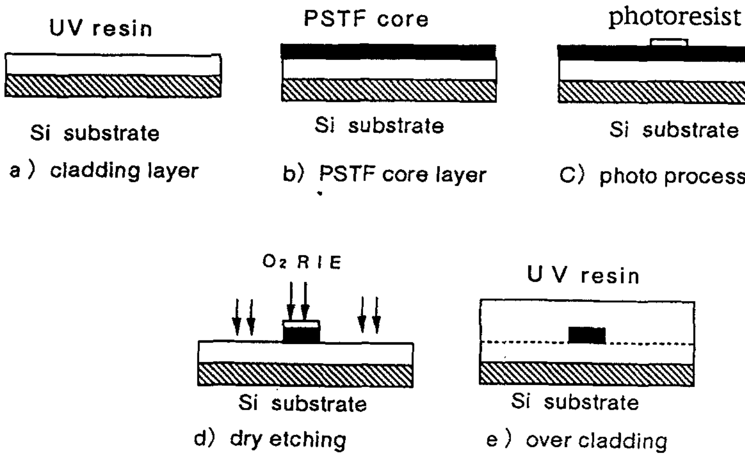


FIGURE 7 Fabrication process of PSTF single mode channel waveguide

For PSTF thin films, single mode channel waveguides were fabricated using the conventional photo-process[10]. $O_2$ reactive ion etching (RIE) technique was used to make the channel. Figure 7 shows the outline of the waveguides fabrication process. First, a planar waveguide was fabricated on a silicon substrate by spin-coating. As a cladding, UV-cured epoxy resin was used. To satisfy the refractive index difference between the core and the cladding to obtain single mode structure, PSTF 44 was used as a core polymer. Refractive index difference between the core and the cladding of the waveguide is 0.011 at 1.3 μm. The thickness of the waveguides could be controlled by spinning condition. The typical thickness was 5 μm. The core ridges were then formed by RIE until the substrate surface was exposed. Finally the core ridges were covered with UV-cured resin. The waveguide has a rectangular core and the cladding polymer completely covers the core ridge. This channel waveguide has 5 μm width, 5 μm height and 2.5 cm length.

TABLE I Waveguide parameters of PSTF 44

| wavelength | d;depth | w; width (increment of 1μm) | refractive index core | Δ n |
|---|---|---|---|---|
| 1.31μm | 5.5μm | from 3.8 to 10.8μm | 1.610 | 0.7% |
| 1.55μm | 5.5μm | from 3.8 to 10.8μm | 1.603 | 0.4% |

Table I shows the parameters of the single mode channel waveguides. In this case, waveguide width was varied by changing the photo-mask for the channel. Figure 8 shows the cross-sectional photograph of PSTF channel waveguides. Figure 8 (a) shows a scanning electron microscope (SEM) photograph of a PSTF ridge waveguide. Figure 8 (b) shows a cross-section photograph of the channel waveguide on silica glass.

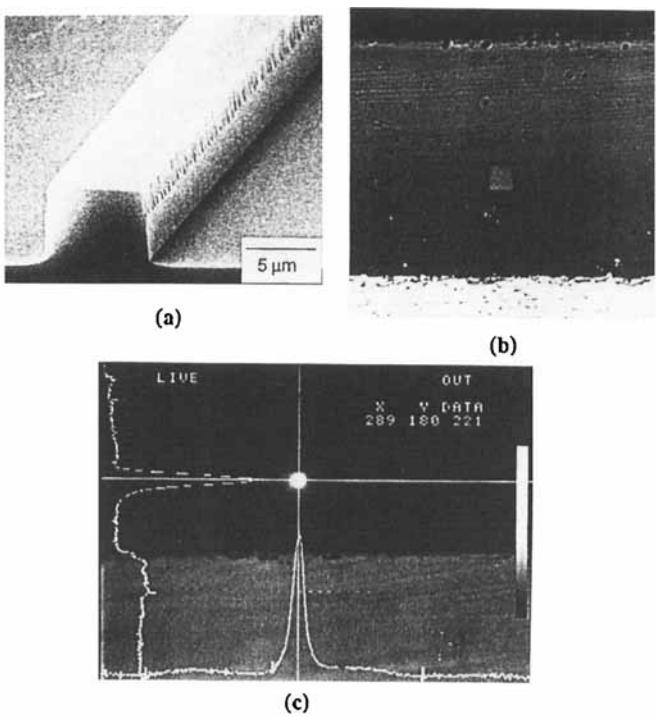


FIGURE 8 (a) SEM photograph of a PSTF ridge waveguide
(b) Cross section photograph of the PSTF channel waveguide
(c) Near field pattern of the guided mode in the PSTF single mode channel waveguide

Near-field pattern for the channel was investigated at wavelength region of 1.3 and 1.55 μm. The pattern was obtained using IR-camera with laser diode as an optical source. Figure 8 (c) shows a near-field pattern of the guided mode of the 1.3 μm wavelength. Figure 9 shows the calculated results for the guided modes based on the value in the Table I. The calculation was based on the method reported by Marcatili. At 1.3 μm, only one waveguide will be a single mode, though, single mode will be up to 7th waveguides (where waveguide width is 9.8 μm) for 1.55 μm wavelength. Measured and the calculate results agree well and the single mode patterns were obtained not only at 1.55 μm but also 1.3 μm wavelength.

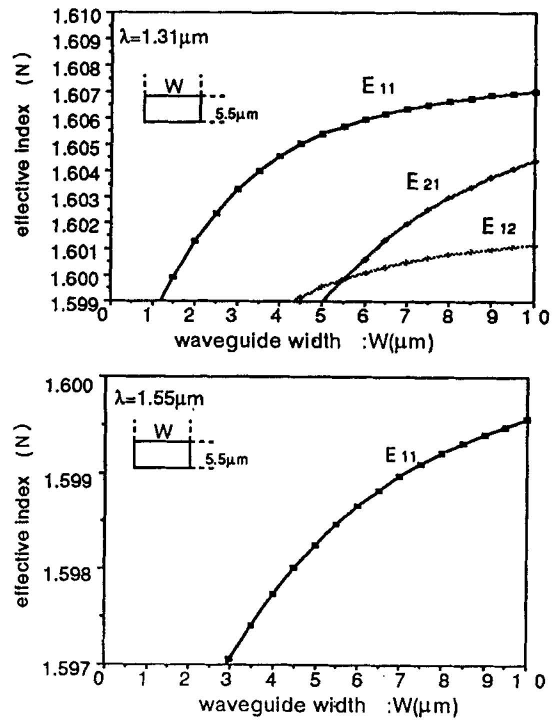


FIGURE 9 Calculated results for the guided mode

Optical losses for the single mode channel at 1.3 and 1.55 μm were 3.5 dB/cm and 4.5 dB/cm, respectively. The loss of the PSTF 44 was about 2 dB/cm low compared to the PSTF 66 waveguide. This was caused due to the reduction of the C-H vibration by controlling the dye contents in the polymer. Loss for the channel waveguide could be decreased by the preparation technique improvement, i. e., narrowing distribution and undercoating with optimal buffer layers.

## CONCLUSIONS

For use as optical switching device, the reduction of the attenuation loss of the organic NLO materials is as much important as the enhancement of $\chi^{(3)}$ value. Novel main-chain polymeric materials with large third-order NLO properties and processabilities are presented. The $\chi^{(3)}$ value of the polymers was estimated to be about $10^{-10}$ esu at 1.55 μm wavelength. NLO polymer core single mode channel waveguides were also fabricated. In this case, high $\chi^{(3)}$ tris-azo-dye was incorporated into fluorinated main-chain polymer. The lowest attenuation losses of the single mode channel waveguide at 1.3 and 1.55 μm were 3.5 and 4.5 dB/cm, respectively. Because these materials have large third-order NLO properties and processabilities, they are suitable for fabricating all-optical devices, i.e., they are promising for ultrafast switches with waveguide devices.

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