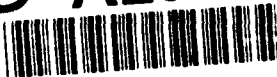


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by

**J. Kumar, S.K. Tripathy, B.K. Mandal, Y.M.
Chen and R.J. Jeng**

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Photoprocessable second-order nonlinear-optical polymers

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Dye-doped polymers and polymers with covalently attached nonlinear-optical (NLO) moieties have demonstrated that large second-order susceptibilities in polymers are achievable.¹⁻³ For practical applications, the stability of $\chi^{(2)}$ at elevated temperatures and the ease of processing into guided wave structures are equally important and need to be addressed. Recently, it has been reported that thermally cross-linked epoxy polymers⁴ are stable at temperatures above 100°C. Thermally crosslinked NLO polymers, however, require several hours of high-temperature curing under a high electric field. This often leads to deterioration of the optical quality of the films.

An alternative route to obtain stable, crosslinked electro-optic polymers by photochemical crosslinking has been developed in our laboratory. In this technique, modified NLO molecules with photocrosslinkable groups are processed with a photocrosslinkable polymer similar to the guest-host system. A photocrosslinking reaction is then performed through common photosensitive chromophores by irradiating UV light during the late phase of poling. Investigations have been carried out with polyvinylcinnamate (PVCN), a commercially available photosensitive polymer, and a new azo dye, 3-cinnamoyloxy-4-[4-(N,N-diethylamino)-cinnamoyloxy phenylazo] nitrobenzene (CNNB-R), synthesized in our laboratory (Fig. 1). This system provides flexibility in processing with different kinds of NLO dyes and exhibits stable second-order nonlinear-optical susceptibility resulting from crosslinking. Furthermore, because the polymer used is a known negative photoresist, it presents significant advantages in the processing and photolithographic patterning steps essential for device fabrication.

Second-order NLO polymers with the NLO units in the polymer backbone have also been synthesized. One of the representative structures is shown in Fig. 2. These polymers are produced by reacting an epoxy with an NLO unit containing an amine group. This prepolymer is subsequently derivatized by using cinnamoyl chloride to provide the photocrosslinking groups. These polymers can be processed, poled, and subsequently photocrosslinked. They also allow incorporation of different types of NLO chromophores. The number density of NLO units in them can be significantly increased. In addition to the cinnamoyl group, which is reactive at 250 nm, styrylacrylate groups have been used, allowing photocrosslinking at 360 nm. The second-order nonlinear coefficients d_{33} have been measured for

the poled, crosslinked system by second-harmonic generation.

The stability of the poled and crosslinked polymers has been investigated by monitoring the decay of the second-harmonic signal. No measurable decay in optical nonlinearity is observed for one of the photocrosslinked polymers up to temperatures of 160°C for several hours. These results are also confirmed by monitoring the stability of the UV-visible absorption spectrum at these temperatures.

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