POLING PROPERTIES OF DOPED FILMS OF TRANSPARENT 
NITROPHENYLTRIAZOLE IN GLASSY POLYMER* 

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DMNPTAz is a newly developed blue-light transparent nonlinear optical material. Poling properties of doped films of DMNPTAz in PSt and PMMA were investigated with electrochromism and waveguiding refractive index measurements, respectively.

Compact and reliable blue coherent light sources are required for high density optical data storage, color image processing and optical measurements. One of possible approach is direct frequency doubling of near infrared semiconductor laser using poled polymer optical waveguides. As was known, four forms of poled polymer films have been studied. Among them, the host-guest doped system, which is formed by dissolving a dopant chromophore in a glassy transparent polymer, is used widely as they can easily be processed to form high quality films.

3,5-Dimethyl-1-(4-nitrophenyl)-1,2,4-triazole1 (DMNPTAz), which possesses higher first hyperpolarizability ($\beta = 12.3 \times 10^{-30}$ esu at 1064 nm, $18.3 \times 10^{-30}$ esu at 830 nm, respectively2) and shorter absorption wavelength ($\lambda_{\text{max}} = 295$ nm, $\lambda_{\text{cut-off}} = 370$ nm) is a promising blue-light transparent nonlinear optical (NLO) material. In this letter the poling properties of doped films of DMNPTAz in polystyrene (PSt) and poly(methyl methacrylate) (PMMA) with electrochromism and waveguiding refractive index measurements were reported.

The doped films were formed by dissolving purified DMNPTAz2 with PSt and PMMA in dichloroethane and spin-coated the solutions onto a microscopic slide or ITO conducting glass substrate. Dopant concentrations were 10–22% by weight ratio of DMNPTAz with polymer, that is, the chromophore densities in doped

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polymer were roughly $3.67 \times 10^{20}$ cm$^{-3}$. The thickness of films were controlled by adjusting the solution viscosity and spin speed and checked by the absorbance of their absorption spectrum. The typical thickness was 1–3 μm. After the coating, the samples were baked overnight under vacuum in a 60°C oven to remove residual solvent. The films were poled with corona or parallel-electrode techniques, respectively. The corona poling apparatus had been described previously.\(^3\) As the poled film’s characterizations, the electrochromic and optical waveguiding techniques were used.\(^4\)

1. Second Order NLO Coefficient $d_{33}$ of Doped Films of DMNPTAz/PS t

Figure 2 shows the absorption spectra of unpoled and poled PS t film doped with DMNPTAz. There are two electrochromic effects on poling: the decrease of peak absorbance and red shift of $\lambda_{\text{max}}$. According to the treatment suggested by Mortazavi,\(^5\) the order parameter $\Phi$ of poled film can be calculated from the observed absorbance before and after poling. When films (chromophore number density $N = 6.7 \times 10^{20}$ cm$^{-3}$) were poled at 60°C, $\Phi$ values were 0.152 (corona poling) and 0.105 (parallel-electrode poling). The average orientation factor $\langle \cos^3 \theta \rangle$ can be determined based on the modified Langevin function approximation,\(^6\) they were 0.30 and 0.25, respectively. From the one-dimensional rigid oriented gas model,\(^5\) which has been widely used to describe the poled polymer films, the second order NLO coefficient $d_{33}$ can be written as:

$$d_{33} = (1/2)N\beta f^2 (f^\omega)^2 \langle \cos^3 \theta \rangle,$$

so the evaluated $d_{33}$ of poled DMNPTAz/PS t doped film was about $3.6-4.3 \times 10^{-9}$ (at 1064 nm) and $5.4-6.5 \times 10^{-9}$ (at 830 nm) esu, respectively.

2. Waveguiding Refractive-Index Measurements of Doped Films of DMNPTAz/PMMA

Page had suggested\(^4\) that a simple method for determining the order parameter $\Phi$ of poled film was to measure the index of refraction for each polarization by the waveguide technique. In a frozen, oriented sample, application of an electric field causes a shift of the charge-transfer band frequency, leading to a change in the refractive index. The shift (for each light polarization) is linearly proportional to the electric field and reaches the value $\delta n_\parallel$ or $\delta n_\perp$ at the poling field $E_p$. The

References
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were controlled by the absorbance of the film doped with the observed absorbance density \( N = \frac{\text{absorbance}}{\text{volume density}} \) can be described as follows:

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\begin{align*}
    r_{13} &= \frac{2}{n^3} \delta n_0 (1 - \Phi) \frac{2\nu_0}{\nu_0^2 - \nu^2} \frac{\delta \nu_\parallel}{E_p}, \\
    r_{33} &= \frac{2}{n^3} \delta n_0 (1 + 2\Phi) \frac{2\nu_0}{\nu_0^2 - \nu^2} \frac{\delta \nu_\parallel}{E_p}.
\end{align*}
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In our samples (\( N = 6.7 \times 10^{20} \text{ cm}^{-3} \), at 90°C poling), \( n = 1.515, \delta n_0 = 0.025, \Phi = 0.13, \nu_0 = 34483 \text{ cm}^{-1}, \delta \nu_\parallel = 353 \text{ cm}^{-1} \) and \( E_p = 1.65 \text{ MV/cm} \). According to the similar treatments with Page, at a wavelength of 532 nm (\( \nu = 18790 \text{ cm}^{-1} \)) and ignoring the local field factor, the electro-optic coefficient of poled DMNPTAz/PMMA doped films can be obtained, i.e. \( r_{33} = 6.4 \text{ pm/V} \) and \( r_{13} = 1.9 \text{ pm/V} \). At a wavelength of 415 nm, the relative values will be about 8.8 and 2.6 pm/V, respectively.

In brief, \( d_{33} \) of doped films of DMNPTAz/PS and electro-optic coefficient \( r \) of doped films of DMNPTAz/PMMA had been evaluated. Although the accuracy of these values is not enough as approximate limitation of the used methods, the above results indicated that DMNPTAz is a promising blue light transparent chromophore for application of second order nonlinear optical effects. When the covalently functionalized copolymers containing DMNPTAz or its analogous side chain were synthesized successfully, it will be suited for generation of blue light from near infra-red semiconductor laser with waveguide geometry.

References