

Photodefinition of channel waveguide in electro-optic polymer

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Abstract: *Polymers with optically active nonlinear chromophores have been shown to have a promising future in low cost and high speed electro-optic device applications. However, a main question of concern is the photochemical stability of the chromophores for long term application. The chromophore TCVDPA with a benzene bridge between a tricyanovinyl acceptor and an amino donor has been reported to have high photochemical stability combined with high electro-optic activity. In the current work direct waveguide definition of the host polymer SU-8, a negative photoresist, containing this chromophore by masked UV exposure followed by development, has been demonstrated. This was possible by utilizing the chromophore low absorption window in the UV region that allows crosslinking of the host polymer by exposing to UV light followed by thermal curing.*

1. Introduction: Over the past decade the demand for the telecommunication services and bandwidth has boomed. To handle this ever increasing demand high speed electro-optic (EO) modulators operating over 100 Ghz are required [1]. The currently used EO modulators based on lithium niobate are limited in their bandwidth to 40 Ghz, because at frequencies higher than this there is a velocity mismatch between the optical wave and the electrical traveling wave leading to dephasing and consequently shorter interaction lengths. To handle such high modulation frequencies a better performing material is definitely required. Nonlinear optical (NLO) polymers have been proposed to be useful candidates for this application already two decades ago [2, 3]. A large second order nonlinear optical susceptibility, low dispersion of dielectric constants, which allows optical waves at infrared frequencies and millimeter waves to co-propagate, and an excellent processability, which the spin coating technique offers yielding highly planar thin films, make NLO polymers promising candidates for telecommunication and data processing applications [4]. Making use of all these advantages polymer EO modulators operating over 100 Ghz have already been demonstrated [5]. With this material the demand for the next generation optical networks can easily be met. Despite all these advantages polymer EO modulators have not yet been commercialized. For long term application three main issues have to be addressed. Firstly, the voltage required to switch a Mach-Zehnder (MZ) from the OFF to the ON state (V_{π}), which is defined by

$$V_{\pi} = \frac{\lambda h}{n^3 r_{33} L \Gamma} \quad (1)$$

Where, λ is the optical wavelength, h is the electrode gap, n is the refractive index, r_{33} is the EO coefficient, L is the interaction length and Γ is the overlap integral of the

electrical and optical waves. Semiconductor electronics demands a V_{π} of less than 1V to avoid the use of expensive amplifiers. V_{π} can be tuned to some extent by varying the geometry of MZ. But for a given configuration V_{π} can only be decreased by increasing r_{33} . Though NLO polymers have the potential for high nonlinearity, the nonlinearity of the individual chromophores does not translate onto a macroscopic scale. This is because there exist electrostatic intermolecular interactions leading to antiparallel clustering of the chromophores during electric field induced poling [6]. The second issue is the photostability of the chromophores at telecommunication wavelengths of 1.3 μm and 1.55 μm . For stable operation the chromophores should not degrade for say 10 years at high optical densities that which might be encountered in the narrow sections of the waveguide channels. Most of the state-of-the-art chromophores which were designed to have high r_{33} coefficients of about 80-100 pm/V cannot also be put to use because they are highly unstable and degrade because of photochemically generated singlet oxygen. To give an idea, the first generation chromophore dimethylaminonitrostilbene (DANS) is stable for 3.5 days and disperse red (DR1) is stable for about 12 days when handling 1 mW optical power at 1.33 μm across a 10 μm^2 cross section [7]. The third important issue is the thermal stability at processing and operating temperatures. The thermal stability of the state of the art chromophores ranges from 250°C to 350°C. The difference between the glass transition temperature of the polymer and the operating temperature, which determines the stability of the poling order, is also important and hence polymers with high glass transition temperature of about 200°C are required.

2. Materials: The chromophore, tricyanovinylidenediphenylaminobenzene (TCVDPA) which was reported to have a high photochemical stability [7], has been employed in the current work. The chromophore consists of a benzene electron bridge between a tricyanovinyl acceptor and a diarylamino donor. The photostability of this chromophore is about two orders of magnitude higher than DANS and its electro-optic activity is about 1.5 times that of DANS. The chromophore was incorporated as guest in the SU8 host. SU8, which is an epoxy-based negative photo resist, is available in different formulations of SU8-2, SU8-25 (for different film thicknesses), etc from Microchem [8]. The formulation SU8-25 is used in our experiments. The solvent used was γ -butyrolactone (GBL). The solution was filtered with a 2 μm filter, spun at 3000 rpm for 20 sec and baked at 95°C for 5 min on a hot plate to give a film thickness of 2 μm .

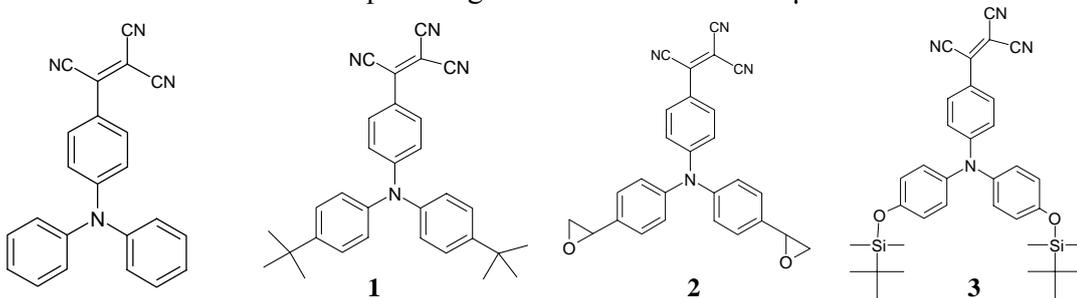


Fig 1: TCVDPA and its modifications with 1. tert-butyl, 2. epoxy and 3. o-tert-butyl-dimethylsilane

The TCVDPA chromophore can be functionalized with bulky side groups as shown in Fig 1. This bulkiness will inhibit closer approach of the chromophores and thereby prevent antiparallel clustering of the chromophores during poling. When equipped with

epoxy molecules as side groups, the chromophores can be anchored to the polymer backbone which will improve temporal stability and also photochemical stability to some extent. The TCVDPA guest-host (GH) system can be poled at 60°C which is the glass-transition (T_g) of the uncured SU8. After poling the T_g of the GH system can be raised to about 200°C by curing making the poling order stable.

3. Experimental results: TCVDPA was incorporated in SU8 as guest-host (GH) polymer. Films with different concentrations of TCVDPA, 5 wt%, 10 wt% and 20 wt% were prepared and the refractive index (n) was measured using Woolam ellipsometer. Fig 2 shows the refractive index of SU8 as a function of the TCVDPA concentration. A linear behavior is observed up to a concentration of 20 wt%. This makes it clear that chromophore segregation does not take place up to 20 wt% of TCVDPA in SU8. This relatively high chromophore concentration is made possible by taking advantage of the fact that SU8 is in the uncrosslinked monomeric state. This is attractive as high concentrations of chromophore can be achieved without segregation problems, which in turn will lead to high nonlinearity, as the NLO properties scale with the chromophore number density. The small deviation from linear behavior at 5 wt% is a measurement error caused by the film thickness that was much larger than what the Woolam ellipsometer demands for accurate measurement of refractive indices in this refractive index range.

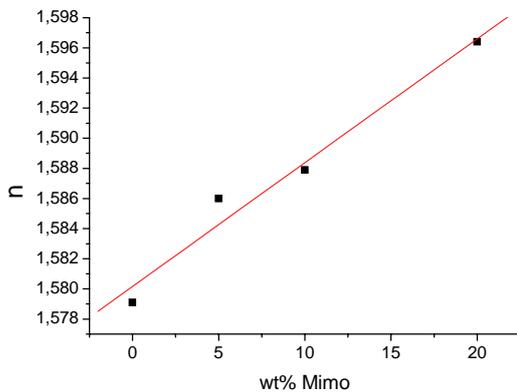


Fig 2: Refractive index of SU8 as a function of TCVDPA concentration measured at 1550 nm

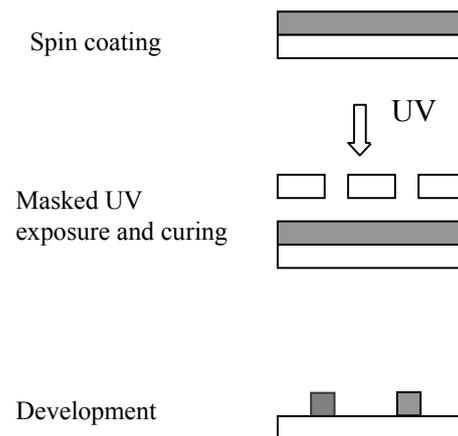


Fig 3: Photodefinition process

Photodefinition of polymers is an attractive fabrication technique for channel wave guides. It is a direct method and much simpler than reactive ion etching which requires a masking layer step. Photodefinition of SU8-TCVDPA GH polymer is demonstrated by exploiting the low UV absorption window of the TCVDPA chromophore shown in Fig 4, in which region most of the other chromophores are highly absorbing. The photo definition process is shown in Fig 3. Fig 5 shows a photo defined channel in SU8 5 wt % TCVDPA on Si substrate. SU8 5 wt% TCVDPA was spun on Si at 3000 rpm to give a film thickness of 2 μm . It was then baked at 95°C for 5 min on hot plate (pre bake). The polymer film is then exposed to UV with a bright field Cr mask for 5 min and cured at 95°C for 5 min (post bake). The dark regions in Fig 5 are crosslinked and SU8 in the

Channel waveguide definition in electro-optic polymers with a novel chromophore by UV-thermal crosslinking

bright channel was uncrosslinked and was removed during development. The channel geometry depends on the exposure time and the post bake time. These parameters can be optimized to have perfect side walls.

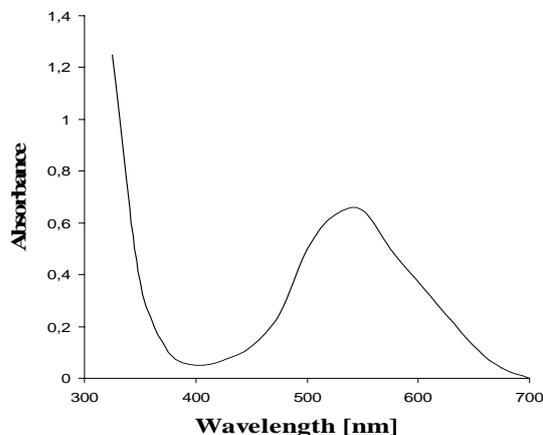


Fig 4: Absorption spectrum of TCVDPA



Fig 5: Photo defined channel in SU8 5 wt% TCVDPA

4. Conclusions: The TCVDPA chromophore has been incorporated as guest in the SU8 polymer. TCVDPA shows good solubility in the GBL solvent and no segregation problems were encountered up to a concentration of 20 wt% in SU8. The SU8-TCVDPA guest host system also shows a good spinning behavior with highly homogenous and planar films. The low UV absorption window of TCVDPA worked as expected, allowing the photo definition of SU8. This system has the advantage that low temperature poling can be done in the uncrosslinked state. Several modifications of TCVDPA with bulky side groups are possible which will enhance the poling efficiency.

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5. References

- [1] Y. Shi, C. Zhang, H. Zhang, J. Betchel, L. Dalton, B. Robinson, and W. Steier, "Low half voltage polymeric electro-optic modulator achieved by controlling chromophore shape", *Science* vol 288, pp 119-122, 2000.
- [2] G. R. Meredith, J. G. Van Dusen, D. J. Williams, *Mocromolecules* Vol 15, pp 1385, 1982.
- [3] D. Cheng, H. R. Fetterman, A. Chen, W. H Steier, W. Wang, Y. Shi, *Appl. Phys. Lett.*, vol 70, pp 3335, 1997.
- [4] L. R. Dalton, W. H. Steier, B. H. Robinson and L. Irwin "From molecules to opto chips", *J. Mater. Chem.*, vol 9, pp 1905-1920, 1999.
- [5] L. R. Dalton, A. Harper, A. Ren, F. Wang, G. Todorova, J. Chen, C. Zhang and M. Lee, "Polymeric Electro-optic modulators", *Ind. Eng. Chem. Res.* vol 38, pp 8-33, 1999.
- [6] B. H. Robinson and L. R. Dalton, "Monte carlo statistical mechanical simulations of the competition of Intermolecular electrostatic and poling field interactions", *J. Phys. Chem A*, vol 104, pp 4785-4795, 2000.
- [7] A. G. Gonzalez, G. I. Stegeman, A. K. Y. Jen, X. Wu, M. Canva, A. C. Kowalczyk, X. Q. Zhang, and H. Z. Lackritz, "Photostability of electro-optic polymers possessing chromophores with efficient amino donors and cyano containing acceptors", *J. Opt. Soc. Am, B* vol 18, pp 1846, 2001.
- [8] www.microchem.com