Photodefinable electro-optic polymer for high-speed modulators

M. Balakrishnan, M. Faccini, M.B.J. Diemeer, W. Verboom, A. Driessen, D.N. Reinhoudt and A. Leinse

Direct waveguide definition of a negative photoresist (SU8) containing tricyanovinylidenediphenylaminobenzene (TCVDPA) as electro-optic (EO) chromophore, has been demonstrated for the first time. This was possible by utilising the chromophore low absorption window in the UV region allowing crosslinking of the host polymer by exposing to UV light followed by thermal curing. TCVDPA was modified by attachment of bulky side groups. This reduced the intermolecular interactions and resulted in an increased EO (r_{33}) coefficient.

Introduction: Over the past decade the demand for 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 LiNbO_3 are limited in bandwidth to 40 GHz, because at higher frequencies the velocity mismatch between the optical wave and the electrical travelling wave yields too large dephasing and consequently too short interaction lengths. To handle such high modulation frequencies a better performing material is required. Second-order nonlinear optical (NLO) polymers [2, 3] were proposed two decades ago as useful candidates for this application. Though NLO polymers have the potential for high nonlinearity, the nonlinearity of the individual chromophores does not translate completely onto a macroscopic scale. This is because electrostatic intermolecular interactions lead to antiparallel clustering of the chromophores during electric field induced poling. These intermolecular interactions can be reduced by modifying the shape of the chromophore (making it more spherical) and thereby preventing their closer approach [4]. For long-term applications the chromophores should have a high photochemical stability at the operating wavelength and a high stability of the poling order at the operating temperature. TCVDPA has the highest reported photochemical stability [5]. In addition, its NLO figure of merit is higher than dimethylaminonitrostilbene (DANS) and disperse red (DR1). The difference between the glass transition temperature (T_g) of the polymer and the operating temperature, which determines the stability of the poling order, requires polymers with a high T_g of about 200°C. When the NLO chromophores are incorporated in a photodefinable polymer, electro-optically active waveguides can be obtained by direct photodefinition. Compared with the reactive ion etching technique, this requires fewer processing steps and yields less sidewall roughness. In this Letter we report for the first time the direct photodefinition of an electro-optic polymer, i.e. TCVDPA in the SU8 host. Improvement of the poling efficiency by modifying TCVDPA with bulky side groups is also presented.

Fig. 1 TCVDPA and its modifications; SU8
a TCVDPA and its modifications b SU8

Materials: The TCVDPA chromophore (Fig. 1a, $R = \text{H}$) was used in the current work. It consists of a single benzene electron bridge between a tricyanovinyl acceptor and a diarylamino donor. For photodefinition, TCVDPA is incorporated as a guest in the SU8 (Fig. 1b) host. TCVDPA with different bulky groups ($R = \text{tert-butyl}$, methoxy (MeO) and *tert*-butyl-dimethylsilane (TBDMS)) were prepared to study the inhibition of the intermolecular interactions. The T_g of uncrosslinked SU8 is 60°C. By crosslinking, the T_g can be raised to about 200°C.

Photodefinition: Photodefinition of the SU8-TCVDPA guest-host (GH) polymer is demonstrated by exploiting the low UV absorption window of the TCVDPA chromophore shown in Fig. 2, in which region most of the other NLO chromophores are highly absorbing. The photodefinition process is shown in Fig. 3. SU8 5 wt% TCVDPA was spun on a Si substrate at 3000 rpm to give a film thickness of 2 μm . It was then baked at 95°C for 5 min on a hotplate (soft bake). Subsequently, the polymer film was exposed to UV light with a Cr contact mask for 5 min in a Karl Süss mask aligner MA55 (365, 405 and 435 nm) and cured at 95°C for 5 min (post-bake). The unexposed regions are uncrosslinked and are removed by development.

Fig. 2 Absorption spectrum of TCVDPA

Fig. 3 Photodefinition process

Poling: The polymer should be noncentrosymmetric in order to exhibit second-order nonlinearity. This is achieved by poling whereby the polymer is heated to its glass transition temperature (T_g) and the chromophores are aligned by applying an electric field typically of the order of 100 V/ μm . Poling was carried out in a crosslinked polymer film and not in a photodefined waveguide in order to have a large poled region for measurement of the r_{33} . A 2 μm -thick SU8 film with 25 wt% TCVDPA was spun on a glass wafer coated with an indium tin oxide (ITO) layer which serves as the bottom electrode for poling. The film was then heated on a hotplate at 95°C for 1 h and in the oven at 95°C for 8 h under vacuum to remove the solvent. The film was exposed to UV light in a Karl Süss mask aligner MA55 for 2 min and cured at 95°C for 15 min. A 100 nm gold layer was sputtered on the polymer as the top electrode for poling. It was observed that when equipped with TCVDPA as guest, the (T_g) of the crosslinked SU8 is reduced considerably owing to the plasticising effect of the chromophores. The T_g of the cured sample was around 45°C. Therefore the sample was poled by heating it to 45°C and applying an electric field of 100 V/ μm . Poling was carried out for about 40 min. The sample was cooled to room temperature and the electric field removed. An r_{33} coefficient of 6 pm/V was measured at 830 nm immediately after poling by the Teng-Man reflection technique [6]. To make a comparative study, the r_{33} coefficient was also measured in a high T_g polymer, polysulfone (PS host) at different wt% of TCVDPA (guest). All the r_{33} values were measured at 830 nm. This was poled at its T_g under similar poling conditions as SU8–25 wt% TCVDPA. The T_g of polysulfone against the wt% of TCVDPA is shown in Fig. 4, which also shows the r_{33} of the PS-TCVDPA measured at different concentrations of TCVDPA. A deviation from the linear behaviour was observed above 15 wt% of TCVDPA. The measured r_{33} was 9 pm/V at 25 wt% TCVDPA. The difference in r_{33} coefficients between SU8–25 wt% TCVDPA

(6 pm/V) and PS—25 wt% TCVDPA (9 pm/V) can be attributed to the fact that the T_g of the cured SU8—25 wt% TCVDPA is so close to room temperature (about 45°C) that the poling order relaxes rapidly when the poling field is removed at room temperature. This can be prevented by equipping TCVDPA with epoxy groups (Fig. 1a, R = epoxy) and crosslinking TCVDPA-epoxy with SU8.

Fig. 4 Measured r_{33} coefficients for different TCVDPA modifications in SU8 and PS at 830 nm

- r_{33} PS - TCVDPA
- ▲ T_g PS - TCVDPA
- - - r_{33} PS - TCVDPA linear fit
- r_{33} SU8 - TCVDPA
- r_{33} PS - TCVDPA—*tert*-butyl
- r_{33} PS - TCVDPA—MeO
- ◄ r_{33} PS - TCVDPA—TBDMS

The poling behaviour of TCVDPA-*tert*-butyl, TCVDPA-MeO, and TCVDPA-TBDMS was studied by incorporating them as guests in PS at concentrations at which the r_{33} of PS-TCVDPA deviates from linear behaviour. The measured r_{33} values are shown in Fig. 4. At 25 wt%, TCVDPA *tert*-butyl shows an enhancement in r_{33} of 5 pm/V, and at 30 wt% TCVDPA-MeO shows an enhancement of 2 pm/V compared with TCVDPA. These data clearly demonstrate the effect of the bulky groups. In the case of TCVDPA-*tert*-butyl the enhancement in r_{33} is even higher than that predicted by the linear fit. This indicates that some intermolecular interactions are already present even at low TCVDPA concentration (<15 wt%) in PS. Contrary to our expectations, at 20 wt% TCVDPA-TBDMS gave an r_{33} of only 2 pm/V compared with 7 pm/V measured with TCVDPA. This can be explained by the high molecular weight of TCVDPA-TBDMS which not only reduces the chromophore number density for a given wt% but also reduces the poling efficiency owing to the restricted motion of the chromophores.

Conclusion: For the first time, photodefinition of an electro-optic polymer has been demonstrated with the SU8—TCVDPA system

using the low UV absorption window of TCVDPA chromophore. The crosslinked polymer system was poled and an r_{33} of 6 pm/V at 830 nm was measured. Increasing the r_{33} by the attachment of bulky groups to the chromophore to inhibit intermolecular interactions was demonstrated.

Acknowledgments: This research work is supported by the Dutch Technology Foundation STW, Applied Science Division of NWO and the Technology Program of the Ministry of Economic Affairs and carried out within the framework of the project TOE 6067 'Broadband and wavelength selective modulators for optical communication based on electro-optic polymers'.

© IEE 2006

6 October 2005

Electronics Letters online no: 20063535

doi: 10.1049/el:20063535

M. Balakrishnan, M.B.J. Diemeer and A. Driessen (*Integrated Optical Microsystems, University of Twente, MESA+ Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands*)

E-mail: m.balakrishnan@ewi.utwente.nl

M. Faccini, W. Verboom and D.N. Reinhoudt (*Laboratory of Supramolecular Chemistry and Technology, University of Twente, MESA+ Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands*)

A. Leinse (*LioniX BV, P.O. Box 456, Enschede 7500 AH, The Netherlands*)

References

- Shi, Y., *et al.*: 'Low half voltage polymeric electro-optic modulator achieved by controlling chromophore shape', *Science*, 2000, **288**, pp. 119–122
- Meredith, G.R., Van Dusen, J.G., and Williams, D.J.: 'Optical and nonlinear optical characterization of molecularly doped thermotropic liquid crystalline polymers', *Macromol.*, 1998, **15**, pp. 1385–1389
- Cheng, D., *et al.*: 'Demonstration of 110 GHz electro-optic polymer modulators', *Appl. Phys. Lett.*, 1997, **70**, pp. 3335–3337
- Robinson, B.H., and Dalton, L.R.: 'Monte Carlo statistical mechanical simulations of the competition of intermolecular electrostatic and poling field interactions', *J. Phys. Chem. A*, 2000, **104**, pp. 4785–4795
- Gonzales, A.G., *et al.*: 'Photostability of electro-optic polymers possessing chromophores with efficient amino donors and cyano containing acceptors', *J. Opt. Soc. Am. B*, 2001, **18**, pp. 1846–1853
- Teng, C.C., and Man, H.T.: 'Simple reflection technique for the measuring the electro-optic coefficient of poled polymers', *Appl. Phys. Lett.*, 1990, **56**, pp. 1734–1736

Copyright of Electronics Letters is the property of IEE and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.